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INFRARED AND RAMAN SPECTRA OF SOME FLUORINATED ETHANES EXHIBITING ROTATIONAL ISOMERISM

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PETER KLABOE

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INFRARED AND RAMAN SPECTRA OF SOME FLUORINATED ETHANES EXHIBITING ROTATIONAL ISOMERISM

APPROVED BY

J. Rud Nielsen

Harold E. Hoagland

DISSERTATION COMMITTEE

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CHAPTER I

INTRODUCTION

For a long time it was believed to be impossible to synthesize molecules of carbon and halogen containing more than three carbon atoms. After the first liquid fluorocarbon was identified,[1] however, fluorocarbons containing more than three carbon atoms per molecule were shown to be extremely stable and unreactive.[2] The extreme electronegativity and the small size of the fluorine atom give the fluorocarbons unique physical and chemical properties. They are in general highly volatile, they have low surface tension and refractive index, and their dielectric constants are lower than those of hydrocarbons with the same carbon skeleton.

The stabilities of the halocarbons are partly expressed by the energies of the carbon-halogen bonds. The bond energy

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[1] J. H. Simons and L. P. Block, J. Am. Chem. Soc. 59, 1407 (1937).

[2] J. H. Simons and L. P. Block, J. Am. Chem. Soc. 61, 2962 (1939).

is considerably higher for fluorine than for the other halogens, and higher than the energy of the carbon-hydrogen bond. Furthermore, the spatial relationships permit a complete covering of the carbon skeleton with fluorine to protect the carbon atoms and the bonds from outside attack. The hydrogen atoms are too small to cover the carbon skeleton effectively in the hydrocarbons, and a shell of chlorine around carbon atoms can exist only under strain. It has been predicted that the stability of the C - F bond will permit the creation of a greater number of compounds in the fluorocarbon domain than in organic chemistry.[3] The fluorocarbons have become very important as industrial products, e.g. as aerosol propellants, lubricants, refrigerants and electrical insulators. Their resistance to strong acids and bases, and to strong oxidizing and reducing agents, and the fact that they are completely non-combustible, may vastly increase their applications in the future.

A number of investigators have studied the molecular structure and properties of fluorocarbons and fluorinated hydrocarbons. Dipole moment,[4,5] electron diffraction,[6]

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[3] J. H. Simons in Fluorine Chemistry, Volume I, page 403 (Academic Press Inc., New York, 1950).

[4] C. P. Smyth et al., J. Chem. Phys. 1, 190 (1933); J. Am. Chem. Soc. 63, 57 (1941).

[5] N. J. Leonard and L. E. Sutton, J. Am. Chem. Soc. 70, 1564 (1948).

[6] F. A. M. Buck and R. L. Livingston, J. Am. Chem. Soc. 70, 2817 (1948).

microwave[7] and thermodynamic[8,9] methods have given valuable information about the structure of these compounds. Extensive studies of the vibrational spectra of fluorine-containing halomethanes have been carried out among others by Glockler and co-workers[10] and by Cleveland et al.[11] At the University of Oklahoma, Prof. J. Rud Nielsen and co-workers have studied the vibrational spectra of a large number of fluorinated ethylenes and ethanes. The infrared and Raman spectra of more than a dozen fluorinated ethylenes have been reported,[12,13] and assignments and thermodynamic properties have been calculated for most of these compounds. More than twenty fluoro- and fluoro-haloethanes with symmetrical end-group[14]

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[7] W. F. Edgell and A. Roberts, J. Chem. Phys. 16, 1002 (1948).

[8] W. F. Edgell and W. E. Byrd, J. Chem. Phys. 17, 740 (1949).

[9] Russel, Golding and Yost, J. Am. Chem. Soc. 66, 16 (1944).

[10] G. Glockler et al., J. Chem. Phys. 8, 897 (1940); 9, 224, 527 (1941); 10, 607 (1942); 7, 278, 382, 553 (1939); 8, 125, 699 (1940).

[11] F. F. Cleveland et al., J. Chem. Phys. 19, 786 (1951); 25, 941 (1956).

[12] J. Rud Nielsen et al., J. Chem. Phys. 18, 326, 485 (1950); 20, 1090 (1952); 23, 1944 (1953); 27, 264 (1957); 30, 98, 103 (1959).

[13] K. Lakshmi, "Vibrational Spectra of CFCl:CHBr, C_2H_2FBr and $CF_2Br - CHBr_2$," (Ph. D. Thesis, University of Oklahoma, 1959).

[14] J. Rud Nielsen et al., J. Chem. Phys. 16, 67 (1948); 18, 1471 (1950); 20, 473, 847 (1952); 21, 383, 1060, 1070 (1953); 23, 329 (1955); 27, 887, 891 (1957); 30, 1375 (1959).

have been studied in this laboratory. Assignments of all of the vibrational fundamental frequencies have been made for most of these molecules, and thermodynamic functions have been calculated for many of these compounds in the ideal-gaseous state.

A very large number of halogenated ethanes having no symmetrical end-group, CX_3, can be synthesized. The study of these molecules is complicated because of the existence of rotational isomerism. Free rotation about the C-C bond, e.g. in ethane, was for a long time assumed to occur, since different isomers analogous to the cis and trans isomers of alkenes had never been isolated. However, it was discovered in 1922 that biphenyls containing bulky substituents in the four ortho-positions can be separated into enantiomorphs.[15] This was interpreted as a restriction on the rotation around the C-C bond. Some years later Kohlrausch[16] postulated the existence of two isomeric forms in the liquid state of 1,2-dichloroethane, in order to explain the large number of observed Raman lines. More recently, the comparison of measured thermodynamic functions with those calculated from statistical mechanics revealed the existence of restricted rotation in C_2H_6 and C_2D_6.[17] Measurements of dipole moments

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[15] G. H. Christie and J. Kenner, J. Chem. Soc. 121, 614 (1922).

[16] K. W. F. Kohlrausch, Z. Physik. Chem. B, 1932 (18) 61.

[17] J. D. Kemp and K. S. Pitzer, J. Chem. Phys. 4, 479 (1936); J. Am. Chem. Soc. 59, 276 (1937).

of substituted ethanes, and the temperature variations of the dipole moments,[18] have confirmed the existence of hindered, rather than free, rotation in these molecules.

It is convenient to regard the potential energy of ethane and substituted ethanes as a function of the rotational angle θ between the end-groups. In the case of completely free rotation the potential energy would be a constant, independent of θ.

Actually the potential energy of ethane is represented by a curve with three identical minima, 120^{o} apart (Fig. 1). The minima correspond to three stable configurations of ethane, and the potential function is roughly given by the expression $E = \frac{1}{2}E_{o}\ (1 - \cos 3\theta)$. It has been found that the three potential minima of ethane corresponds to the "staggered" configurations (Fig. 2,a), while the "eclipsed" configurations (Fig. 2,b) are unstable.

Among halogen substituted ethanes, molecules of the general structure $CX_2Y - CX_2Y$ have been extensively studied. Early investigators believed $CH_2Cl - CH_2Cl$ to exist in two isomeric forms, one of symmetry C_{2h} ("staggered" or trans), (Fig. 3,a) and one of symmetry C_{2v} ("eclipsed" or cis), (Fig. 3,b). Later work with electron diffraction[19] and particularly the extensive researches by different physical

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[18] C. P. Smyth, Dielectric Behavior and Structure (McGraw-Hill Book Company, Inc., New York, 1955).

[19] V. Schomaker and D. P. Stevenson, J. Chem. Phys. 8, 637 (1940).

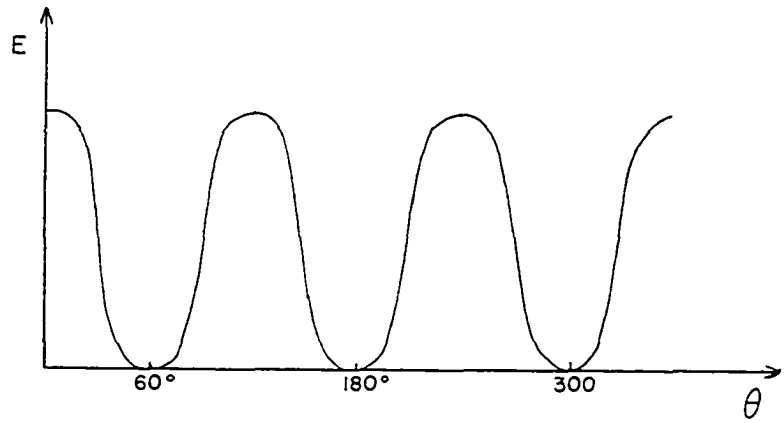
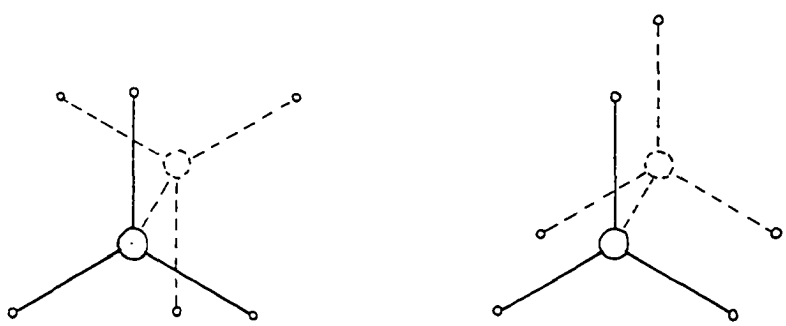


Fig. 1. Potential Enery Curve of Ethane



(a) (b)

Fig. 2. Stable and Unstable Configurations of Ethane

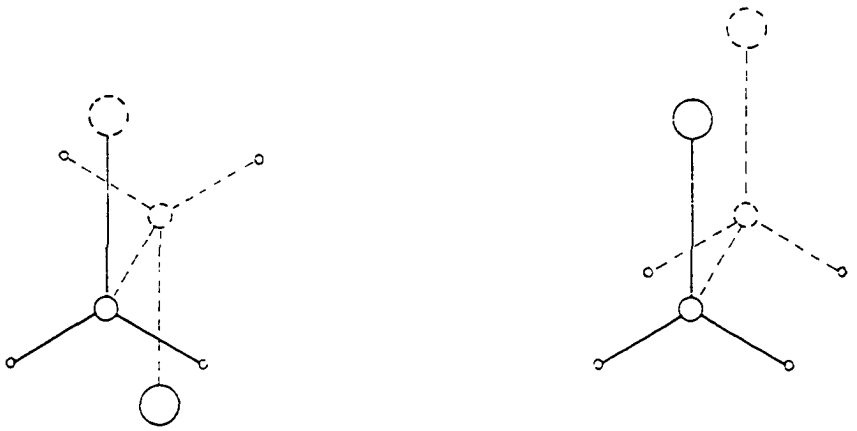


Fig. 3. Stable and Unstable Configurations of Molecules of Structure $CX_2Y\text{-}CX_2Y$

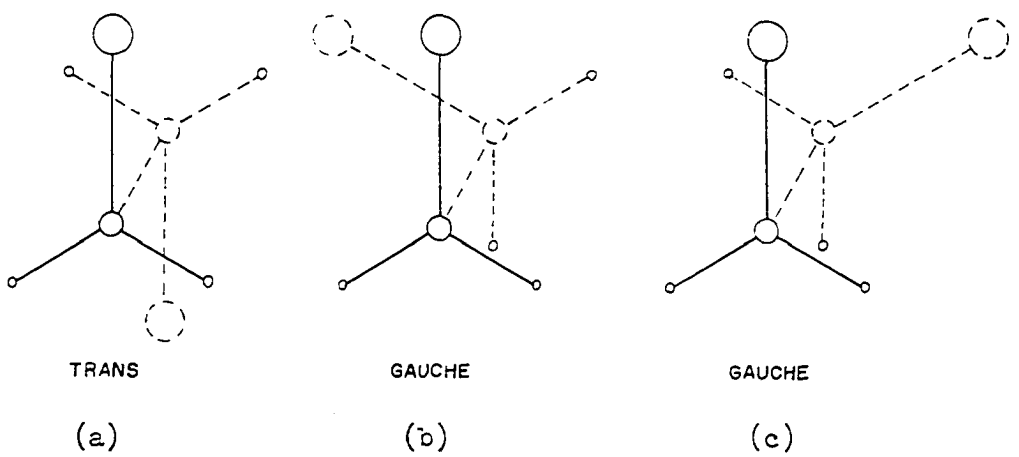


Fig. 4. <u>trans</u> and <u>gauche</u> Configurations of Molecules of Structure $CX_2Y\text{-}CX_2Y$

methods by Mizushima and co-workers,[20] have definitely ruled out the cis-form. $CH_2Cl - CH_2Cl$ has been shown to exist in the gaseous and liquid states as an equilibrium mixture of the trans form of symmetry C_{2h} and two enantiomorphic forms of symmetry C_2, usually called gauche (Fig. 4, a, b, c). A considerable number of halogenated ethanes have been studied by different physical methods with special reference to rotational isomerism. The large amount of information available about these molecules seems to be consistent with the assumption that they exist in staggered configurations only.

An ethane, CXYZ - CX'Y'Z' substituted with 6 different atoms should, according to the theory, exhibit a very complicated isomerism. In addition to the isomerism caused by hindered rotation, there is, because of the presence of two asymmetrical carbon atoms a complicated stereoisomerism with pairs of enantiomorphs and diastereomers. The high complexity of these molecules have prevented research workers from studying them. Nearly all work on rotational isomerism has dealt with molecules of the form $CX_2Y - CX_2'Y'$, and the molecules studied in chapters V - VII of this thesis all belong to this group. These molecules should have one isomer of symmetry C_s and two enantiomorphic isomers of symmetry C_1. Apart from their action on linearly, polarized light, the

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[20] S. I. Mizushima, Internal Rotation and Molecular Structure (Academic Press, Inc., Publishers, New York, 1954).

enantiomorphs have the same physical and chemical properties and identical vibrational spectra. On the other hand, the vibrational spectra of isomers of symmetry C_s and C_1 should be different. It is found, however, that because of the close structural and dynamical similarity between these isomers, an appreciable number of infrared and Raman bands overlap in many cases and cannot be separated with prism instruments.

In substituted ethanes having a symmetrical end-group, all the three "rotational isomers" corresponding to the three staggered configurations will be identical. The study of the vibrational spectra of these molecules is accordingly much simpler than that of molecules without a symmetrical end-group.

Although more than one stable configuration generally occurs in the gaseous and liquid states of ethanes having no symmetrical end-group, many cases are known in which only one form exists in the crystalline phase. In these cases the vibrational spectra of the crystalline solid are much simpler than those of the liquid and gas. This phenomenon was first inferred by Mizushima[20] from the Raman spectrum of 1,2-dichloroethane and has later been used by a number of investigators as an aid in the study of similar compounds. As a result of the present and other work recently carried out in this laboratory[13,21] it may be inferred, however, that

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[21] J. Rud Nielsen and C. J. Halley, to be published.

the existence of more than one isomer in the solid state is more common than generally expected, at least among fluorinated ethanes.

The potential curve for substituted ethanes is not as well known as that for ethane itself (Fig. 1). Molecules of the type $CX_2Y - CX'_2Y'$, are expected to have potential curves as indicated qualitatively in Fig. 5, a, b. Each curve contains three minima corresponding to three isomeric forms. The spacing between two minima will in general not be exactly 120°, but because of the assumed molecular structure, the curves must be symmetrical around $\theta = 180°$. The stable isomers of symmetry C_s and C_1 will here be designed as "trans" and "gauche," respectively. The terms trans and gauche (without quotation marks) will be reserved for isomers of symmetry C_{2h} and C_2 of molecules with the general structure $CX_2Y - CX_2Y$. In Fig. 5,a, the "gauche"-forms have lower energy, i.e., are more stable, than the "trans"-form. The opposite is true in Fig. 5,b. Important parameters of the potential curves are the following: θ, the angle between the potential minima; ΔE_o^o, the energy difference between the stable isomeric forms extrapolated to 0°K; B the potential barrier opposing a transition from "trans" to "gauche"; and B', the potential barrier between the two enantiomorphic "gauche"-forms. θ can be determined by electron diffraction, B and B' can most accurately be determined by microwave methods, and ΔE_o^o can be determined by measuring the relative

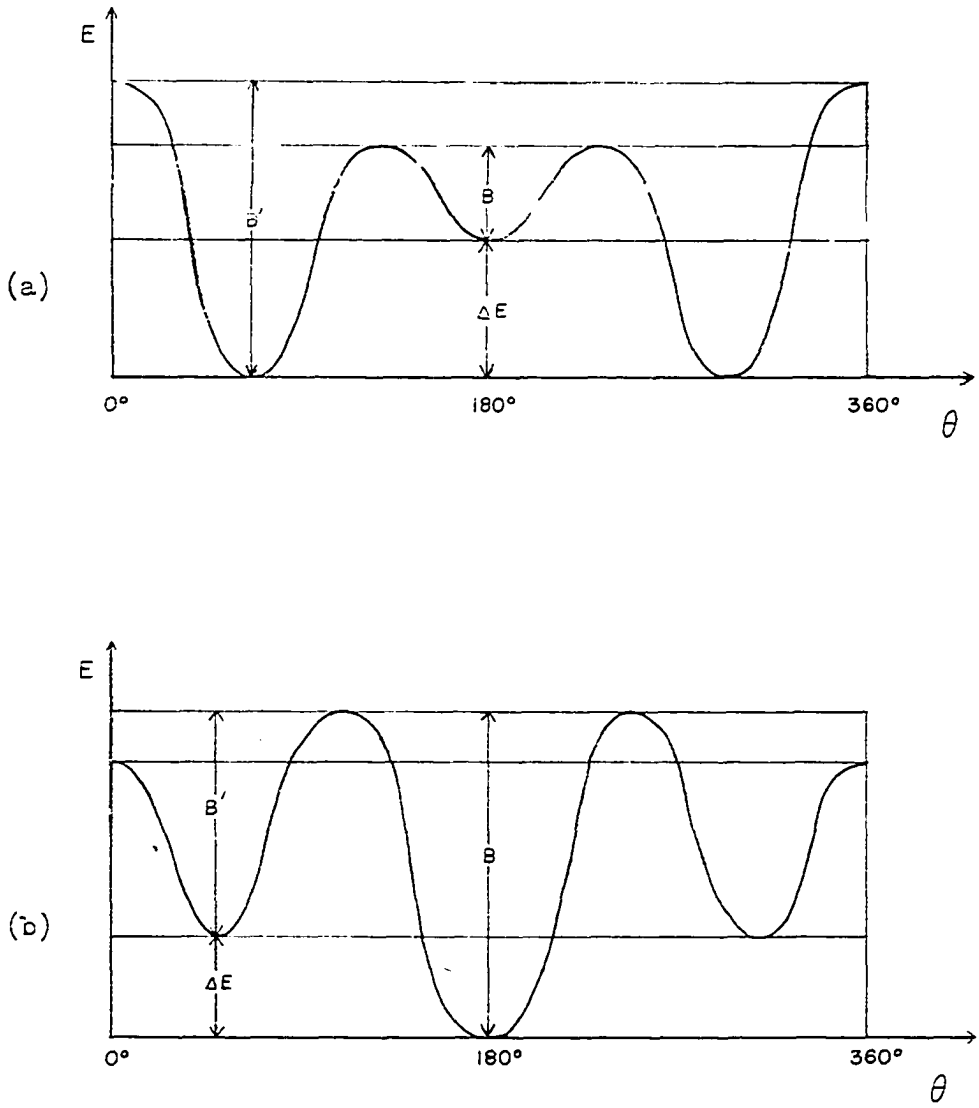

Fig. 5. Potential Energy Curves of Molecules of Structure $CX_2Y\text{-}CX'_2Y'$

amounts of the "trans"- and "gauche"-isomers in equilibrium at different temperatures. Two extreme cases may be considered: (a) B and B' are approximately equal to zero. In this case there is essentially free rotation. (b) B is very large, while the value of B' can have any value. In this case the rotation is frozen out at ordinary temperatures much as in the case of cis and trans isomers of substituted ethylenes. Most halogenated ethanes represent intermediate cases. If B and B' are smaller than 0.6 kcal/mole, the rotation is practically free; if B and B' are larger than 20 kcal/mole, the rotation is practically frozen out at room temperature.[22] One may infer that for rotation about a single bond between two saturated carbon atoms, the activation energy is always less than 20 kcal/mole, since no isomers of this type have been isolated in the gaseous or liquid states.[22] In ethane the activation energy is calculated to be about 3 kcal/mole,[17] and in halogenated ethanes it is probably less than 10 kcal/mole.

When the potential barrier B is fairly low, the equilibrium between the rotational isomers is approximately determined by the classical distribution law. For the ideal gaseous state:

$$(1)\quad \frac{a_{trans}}{a_{gauche}} = \frac{N_{trans}}{N_{gauche}} = \text{const} \times \frac{A_{trans}}{A_{gauche}}$$

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[22] G. H. Wheland, Advanced Organic Chemistry (John Wiley and Sons, Inc., New York, 1953).

where a_{trans} and a_{gauche} are the activities, N_{trans} and N_{gauche} are the numbers of molecules, A_{trans} and A_{gauche} are the intensities of the infrared (or Raman) bands, of trans and gauche, respectively. The equilibrium is determined by the expression,

$$(2)\quad \frac{N_{trans}}{N_{gauche}} = \text{const} \times e^{-\frac{\Delta H^o}{RT}}$$

ΔH^o is the difference in standard enthalpy between the isomers, R is the gas constant, and both are measured in cal/mole. T is the temperature in degrees Kelvin. Substitution of equation (1) in (2) gives,

$$(3)\quad \frac{A_{trans}}{A_{gauche}} = \text{const} \times e^{-\frac{\Delta H^o}{RT}}$$

The methods of statistical thermodynamics give the following correlation,

$$(4)\quad \frac{N_{trans}}{N_{gauche}} = \frac{f_{trans}}{2 \cdot f_{gauche}} \times e^{-\frac{\Delta E_o^o}{RT}}$$

where f_{trans} and f_{gauche} are the partition functions of the trans and gauche forms, respectively. The factor 2 is caused by the existence of two gauche forms but only one trans form. ΔE_o^o is the standard energy difference between the isomers extrapolated to 0^o K (Fig. 5). Assuming the rigid rotator and harmonic oscillator approximations[23]

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[23] G. Herzberg, Infrared and Raman Spectra of Polyatomic Molecules (D. Van Nostrand Company, New York, 1945).

$$(5)\quad \frac{f_{trans}}{f_{gauche}} = \left[\frac{(I_A\ I_B\ I_C)\ trans}{(I_A\ I_B\ I_C)\ gauche}\right]^{\frac{1}{2}} \frac{\prod_i (1 - e^{-\frac{h\nu_i}{kt}})^{trans}}{\prod_i (1 - e^{-\frac{h\nu_i}{kt}})^{gauche}}$$

where $(I_A\ I_B\ I_C)$ trans is the product of the principal moments of inertia of the trans, $(I_A\ I_B\ I_C)$ gauche that of the gauche molecule. ν_i^{trans} and ν_i^{gauche} are the fundamental frequencies of the trans and gauche, respectively.

From equation (3) it is evident that a plot of $\ln \frac{A_{trans}}{A_{gauche}}$ vs. $1/T$ gives H^o/R. The value of ΔH^o can therefore be readily calculated from the infrared or Raman intensity data obtained at different temperatures. Because

$$(6)\quad \Delta H^o = \Delta E^o + P\Delta V + V\Delta P$$

and since there is no change in pressure or volume at the transition from trans to gauche, $\Delta H^o = \Delta E^o$. In order to evaluate ΔE_o^o from equations (1), (4) and (5), the frequencies of the fundamentals have to be known. In the temperature range of interest, frequencies greater than 1000 cm^{-1} contribute very little to the vibrational partition function, while the low frequencies make a great contribution. The values of the lowest fundamental frequencies, which can be measured in the Raman spectrum only, are often rather uncertain because of strong background radiation from the exciting mercury line. Calculations of ΔH^o have been made in this thesis, but no attempts have been made to calculate ΔE_o^o.

The method of calculating ΔH^o from the temperature

dependence of the intensities of pairs of Raman or infrared bands was first employed by Langseth and Bernstein[24] and later by Rank and co-workers.[25] The method has later been applied by different investigators, among them Bernstein,[26] Mizushima,[20] and Kagarise,[27] to a number of halogenated ethanes. Bernstein and co-workers have also determined these energy differences for halogenated ethanes from measurements made in dilute solutions.[28] Furthermore, the equilibrium amounts of the two isomers can in some cases be determined in the gaseous and liquid states by dipole[18,20] or electron diffraction methods, and ΔH^{o} can be calculated.

Of particular interest for the present work is the research done by Kagarise and Daasch,[29] by Kagarise,[27] and more recently by Lakshmi[13] and Halley[21] in this laboratory; all of these investigators have studied fluorinated ethanes having no symmetrical end-group.

In this thesis a detailed study is made of the

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[24]A. Langseth and H. J. Bernstein, J. Chem. Phys. 8, 410 (1940).

[25]D. H. Rank et al., J. Chem. Phys. 16, 704 (1948); 17, 83, 1349, 1354 (1949).

[26]H. J. Bernstein et al., J. Chem. Phys. 17, 258 (1949); 18, 897 (1950); Can. J. Chem. 35, 734 (1957).

[27]R. E. Kagarise, J. Chem. Phys. 23, 207 (1955); 24, 300, 1264 (1956); 26, 380 (1957); 29, 680 (1958).

[28]H. J. Bernstein et al., J. Am. Chem. Soc. 73, 1815 (1951); 74, 1859 (1952).

[29]R. E. Kagarise and L. W. Daasch, J. Chem. Phys. 23, 113, 130 (1955).

following ethanes: CHF_2 - CHF_2, CH_2F - CH_2F, CF_2Cl - CHF_2, CF_2Br - CHF_2, CF_2Cl - $CFCl_2$ and CF_2Br - CCl_2Br. The work is a part of an extensive investigation of the infrared and Raman spectra of fluorinated ethanes and ethylenes.[12,14] The emphasis has been placed partly on assignments and interpretations of the spectra and partly on the study of the rotational isomerism. The complete assignment of the fundamental vibrational frequencies of molecules having rotational isomerism is very complicated, however, and has been previously attained only for CH_2Cl - CH_2Cl[30] and $CHCl_2$ - $CHCl_2$.[31] In the present study, complete assignments are made of CHF_2 - CHF_2 and CH_2F - CH_2F, but with considerably more uncertainties than in the corresponding work on molecules having symmetrical end-groups.[14] The vibrational spectra of the other molecules could only be partially interpreted. All the molecules studied exhibited rotational isomerism. The relative stabilities of the isomers in the gaseous and liquid states were studied for all of these molecules except CF_2Br - CCl_2Br. Since each of these compounds presents different problems, the work done on each compound and the results obtained are discussed in separate chapters.

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[30] J. Nakagawa and S. I. Mizushima, J. Chem. Phys. 21, 2195 (1953).

[31] J. P. Zietlow, F. F. Cleveland and A. G. Meister, J. Chem. Phys. 24, 142 (1956).

CHAPTER II

EXPERIMENTAL

Infrared Spectra

All the infrared data reported in this study were obtained with the aid of a Perkin-Elmer Model 112 double-pass spectrometer and a Leeds and Northrup recorder. The spectrometer was equipped with prisms of CsBr, NaCl and LiF for use in the various spectral regions. During the course of this work a high-sensitive thermocouple manufactured by Charles M. Reeder and Company was installed, having more than twice the sensitivity of the original thermocouple.

Since the spectrometer is a single beam instrument, atmospheric water vapor and carbon dioxide present in the optical path will produce absorption lines or bands superposed on the spectrum of the sample. The spectrometer was flushed with dry nitrogen to reduce the intensity of the water lines and carbon dioxide bands, but they could not be completely eliminated.

The transmittance due to the sample at any point in the transmission curve was obtained in the following way. The absorption curve (I_0-curve) with the cell empty was first

obtained. Then the absorption curve with the sample in the cell was recorded (I-curve), superposed on the I_0-curve. This was most conveniently done by rolling the recording paper back and starting the I-curve at the same position as the I_0-curve. The zero transmission line was recorded with the slits closed. A Gerber variable scale was used to read off the percentage of energy transmitted at any wave length. When the zero and one-hundred percent transmission marks on this scale coincide with the zero and I_0-curves the reading on the I-curve gives the percent transmission directly.

A number of different absorption cells were used to obtain the absorption spectra in the gaseous phase. A multiple-reflection cell of 1-m path length, fitted with KRS-5 windows was used in some cases. If the samples had sufficiently high vapor pressures at room temperature, better resolution was often obtained by using a 10-cm cell with KBr windows or a 6-cm cell with KRS-5 windows. The gaseous absorption spectra at higher temperatures were obtained with an electrically heated cell made of brass. It was constructed by C. J. Halley and has been described by Lakshmi.[13]

The absorption spectra of the liquids were obtained with sealed cells of different thicknesses. Some of these cells were manufactured by the Perkin-Elmer Corporation, others were constructed in this laboratory.[32]

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[32]D. C. Smith and F. C. Miller, J. Opt. Soc. Am. 34, 130 (1944).

A low-temperature cell was designed by Halley and the author for obtaining absorption spectra in the solid state, at dry-ice and liquid air temperatures. This cell is somewhat similar to that described by Lord and co-workers.[33] Its construction and use have been described in detail by Lakshmi.[13]

Raman Spectra

The Raman spectra were photographed with one or the other of two Applied Research Laboratories 3-prism glass spectrographs. The reciprocal linear dispersion is 15 A/mm at 4358 A and 34 A/mm at 5000 A. All the Raman spectra were obtained of the samples in the liquid state, the samples being contained in sealed Raman tubes made of pyrex glass. The irradiation apparatus has been described by Claassen[34] and Hudson.[35] Eastman Kodak Royal Pan sheet film was used in most cases. It was developed for 12 minutes in Kodak DK-60a developer at 18°C. In some cases Kodak Royal X Pan sheet film was used. This film is approximately 8 times faster than Royal Pan but is more coarse-grained and has less contrast. An iron arc spectrum was photographed adjacent to each Raman spectrum. Prints

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[33] R. C. Lord, R. S. McDonald and F. A. Miller, J. Opt. Soc. Am. 42, 149 (1951).

[34] H. H. Claassen, "Raman Spectra of Some Fluorinated Hydrocarbons" (Ph. D. Thesis, University of Oklahoma, 1949).

[35] R. L. Hudson, "Raman Spectra of Some Fluorinated Aromatics" (Ph. D. Thesis, University of Oklahoma, 1949).

were made from the Raman films, approximately 22.5 times linearly enlarged. The frequencies of the Raman bands were determined by interpolation from the iron lines, with the aid of a large scale calibration curve.[34,35]

The polarization data were obtained from Raman exposures made according to the double exposure method of Crawford and Horwitz.[36] The apparatus and the experimental details have been described by Claassen.[34] A Leeds and Northrup photoelectric recording microphotometer was used to obtain the intensity data from the Raman and stepsector exposures.

The Raman spectra of the compounds in the liquid state at low temperatures (-25° to -80°C) were obtained by a method described by Jackson.[37] The Raman tube was enclosed in a double-walled vacuum jacket. A continuous flow of nitrogen cooled by passing it through a copper coil immersed in liquid air was led into the vacuum jacket. By regulating the flow of nitrogen, the temperature inside the jacket could be maintained at the desired temperature. The latter was measured by means of a calibrated thermocouple. It was not possible to avoid a considerable temperature gradient along the Raman tube.

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[36] B. L. Crawford, Jr. and W. Horwitz, J. Chem. Phys. 15, 882 (1947).

[37] J. A. Jackson, Jr., "Vibrational Spectra of Lead Alkyls" (Ph. D. Thesis, University of Oklahoma, 1955).

CHAPTER III

INFRARED AND RAMAN SPECTRA OF CHF_2 - CHF_2

Introduction

The vibrational spectra of a number of halogenated ethanes having asymmetrical end-groups have been studied with special reference to rotational isomerism,[20,27,29,38] but complete assignments of fundamental vibrational frequencies have been made only for CH_2Cl - CH_2Cl[30] and $CHCl_2$ - $CHCl_2$.[31] In the present chapter infrared and Raman spectral data are reported for CHF_2 - CHF_2, the rotational isomerism exhibited by this compound in the gaseous and liquid states is studied, all vibrational fundamentals for the gauche form and all but the two lowest fundamentals for the trans form are assigned, and the spectra are interpreted in detail.

Experimental Results

The sample (bp -16°C at 746 mm pressure) was prepared and purified in the laboratory of Professor A. L. Henne at Ohio State University. The spectra indicate that the purity

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[38] J. K. Wilmshurst and H. J. Bernstein, Can. J. Chem. 35, 734 (1957).

is high. The infrared absorption spectrum of the gas at room temperature was recorded with the aid of a Perkin-Elmer Model1 112 spectrometer equipped with CsBr, NaCl and LiF prisms and 6- and 10- cm cells. To study the rotational isomerism, the infrared spectrum of the gas in an electrically heated 10-cm cell was obtained also at 70°, 110°, 140° and 170°C. Moreover, the infrared spectrum of the crystalline solid at -170°C was recorded by means of a low-temperature cell somewhat similar to that described by Lord et al.[33] The Raman spectrum of the liquid in a sealed Raman tube at 20°, -25°, and - 80°C, was photographed with an Applied Research Laboratories 3-prism glass spectrograph of reciprocal linear dispersion 15 A/mm at 4358 A. Polarization measurements were made by the method of Crawford and Horwitz.[36] The infrared spectra are shown in Figs. 6-11, and the wave numbers of the observed absorption maxima (or in some cases "shoulders") are listed in Table I. The Raman spectral data are presented in Table II.

Interpretation

The large number of strong bands observed indicates that the compound exists as a mixture of rotational isomers. The fact that a number of strong bands present in the infrared spectrum of the gas are absent in the Raman spectrum, and vice versa, suggests that one of the isomers has the molecular symmetry C_{2h} or the so-called trans form. Its normal vibrations divide into symmetry species in the following manner:

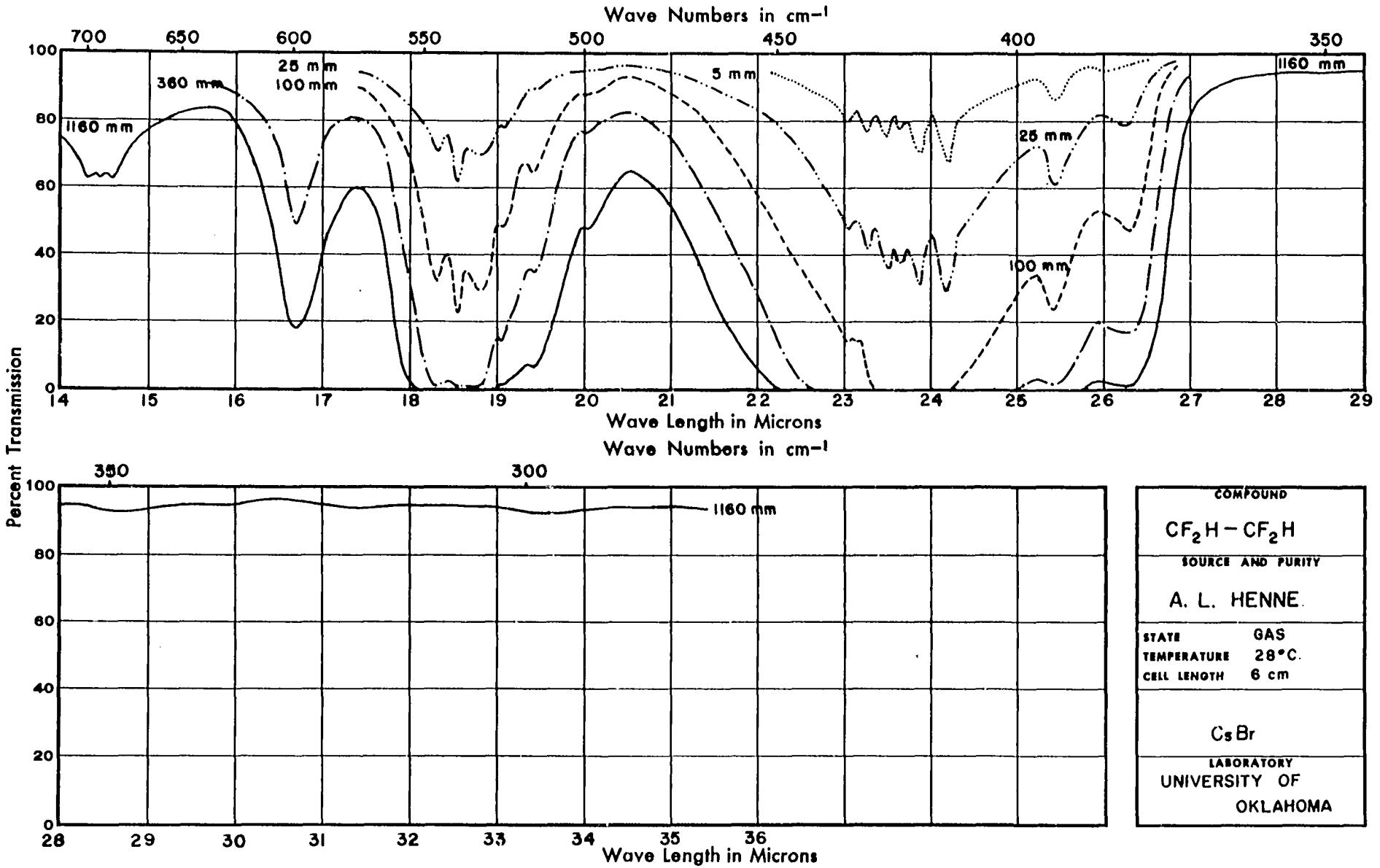

Fig. 6. Infrared Spectrum of Gaseous CHF_2-CHF_2 (CsBr-Region)

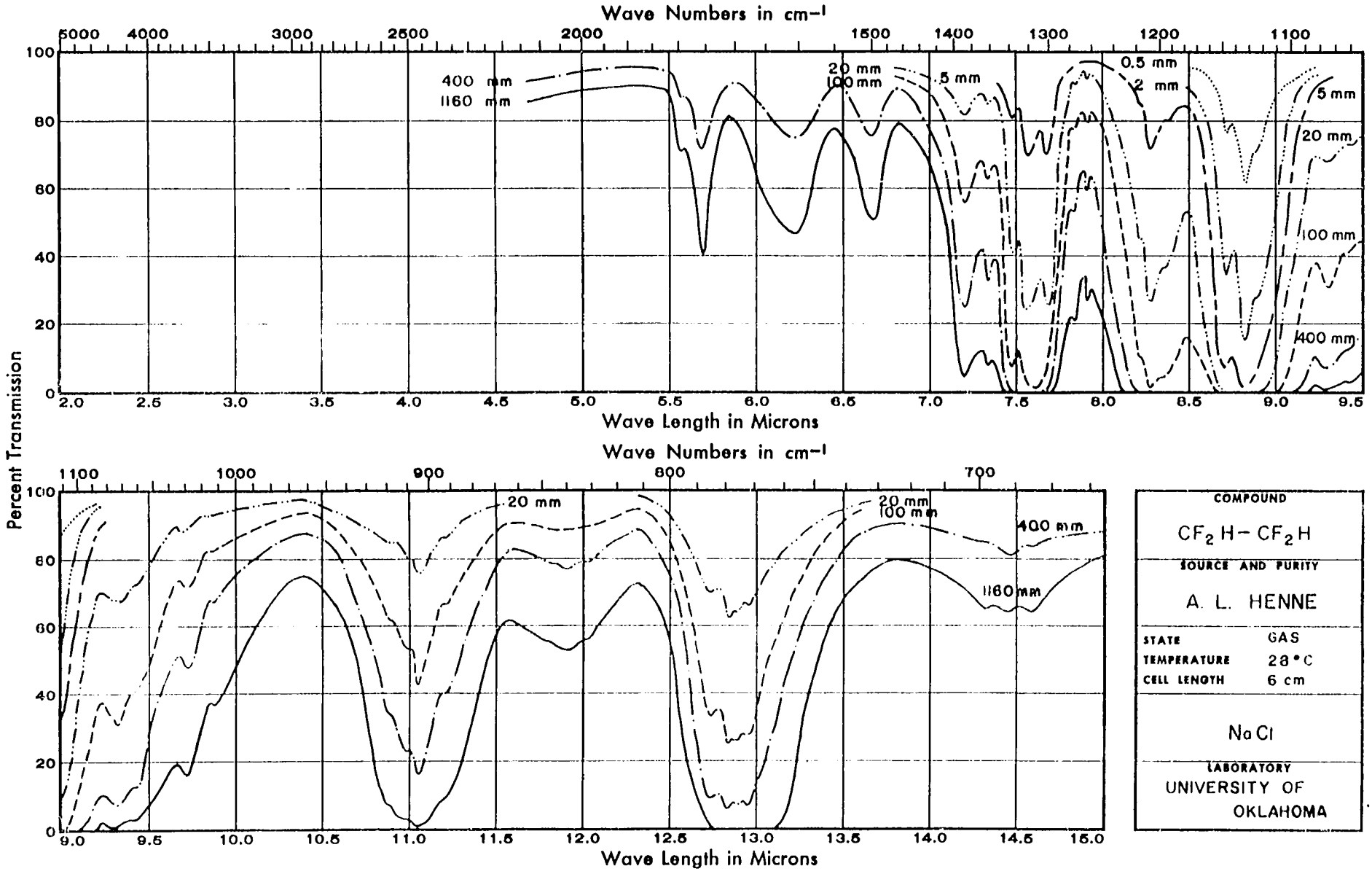

Fig. 7. Infrared Spectrum of Gaseous CHF_2-CHF_2 (NaCl Region)

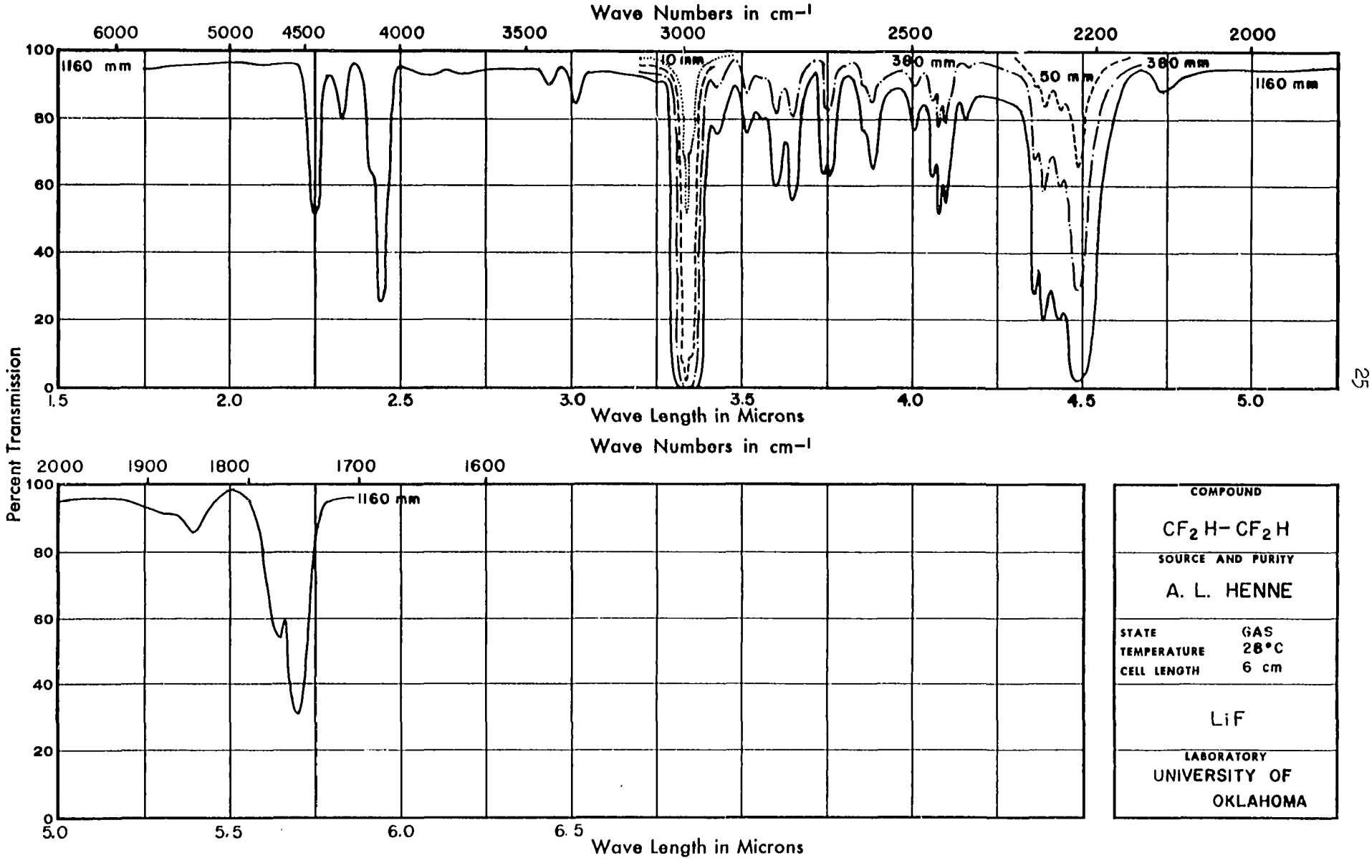

Fig. 8. Infrared Spectrum of Gaseous CHF_2-CHF_2 (LiF Region)

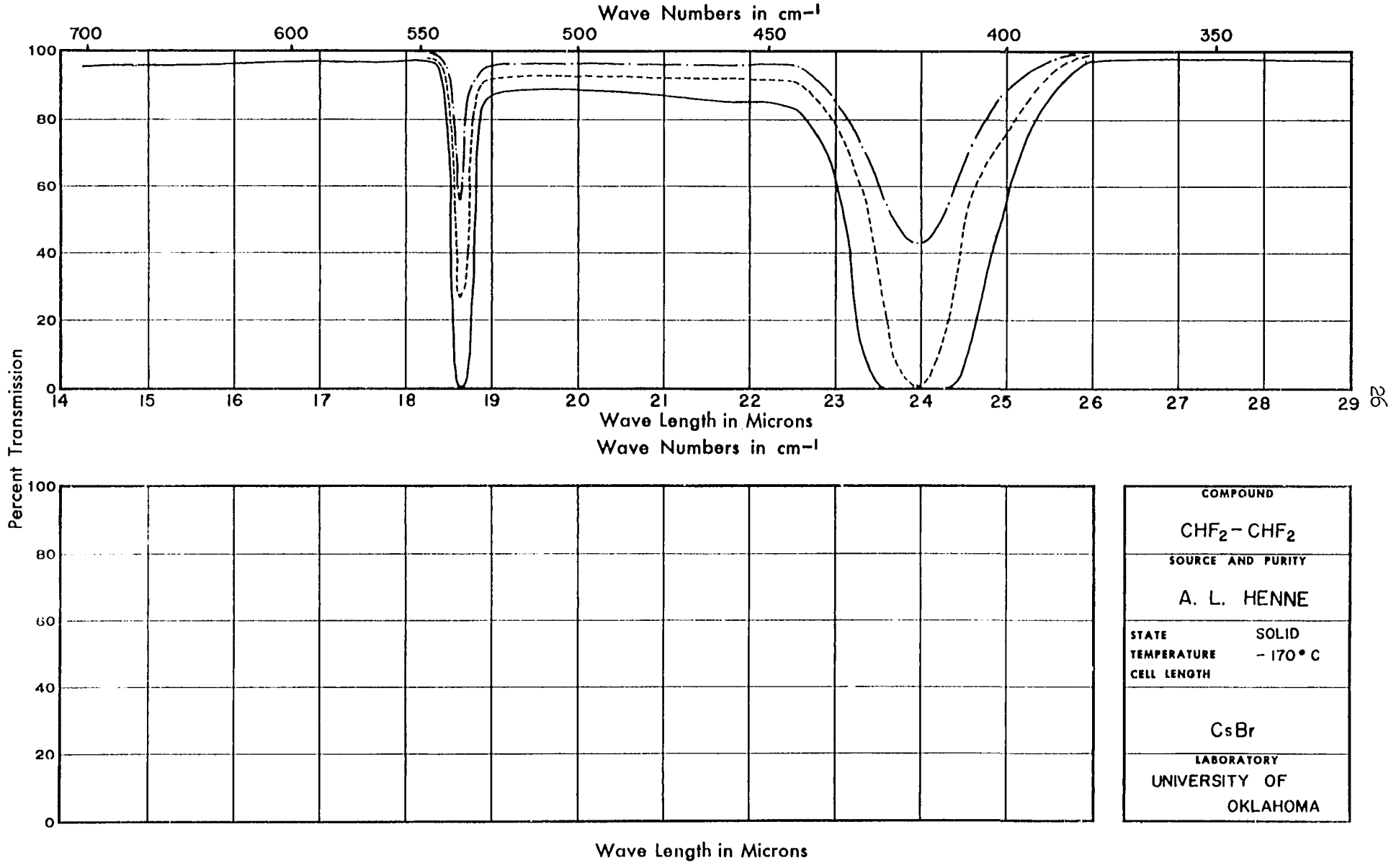

Fig. 9. Infrared Spectrum of Solid CHF_2-CHF_2 (CsBr Region)

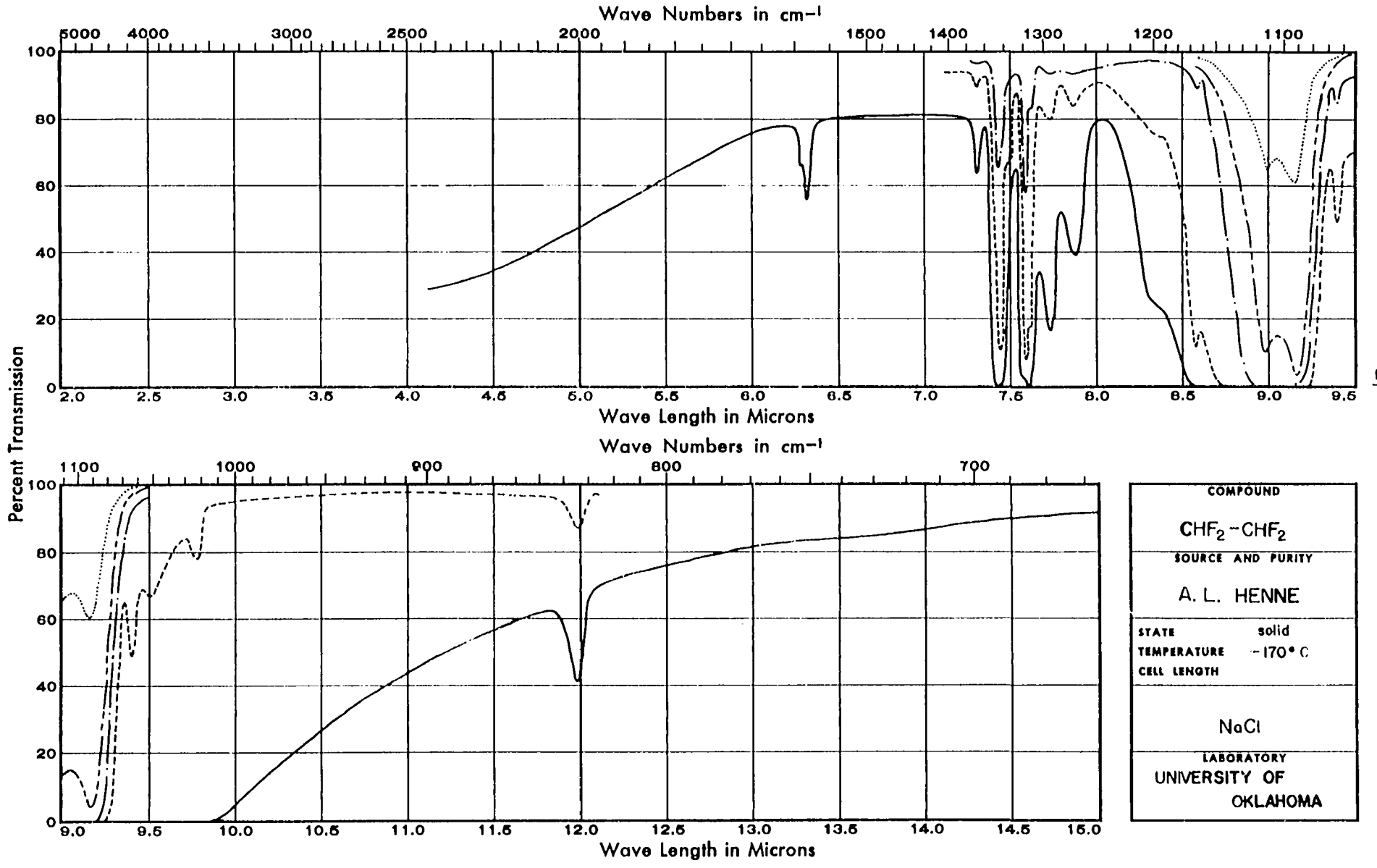

Fig. 10. Infrared Spectrum of Solid CHF_2-CHF_2(NaCl Region)

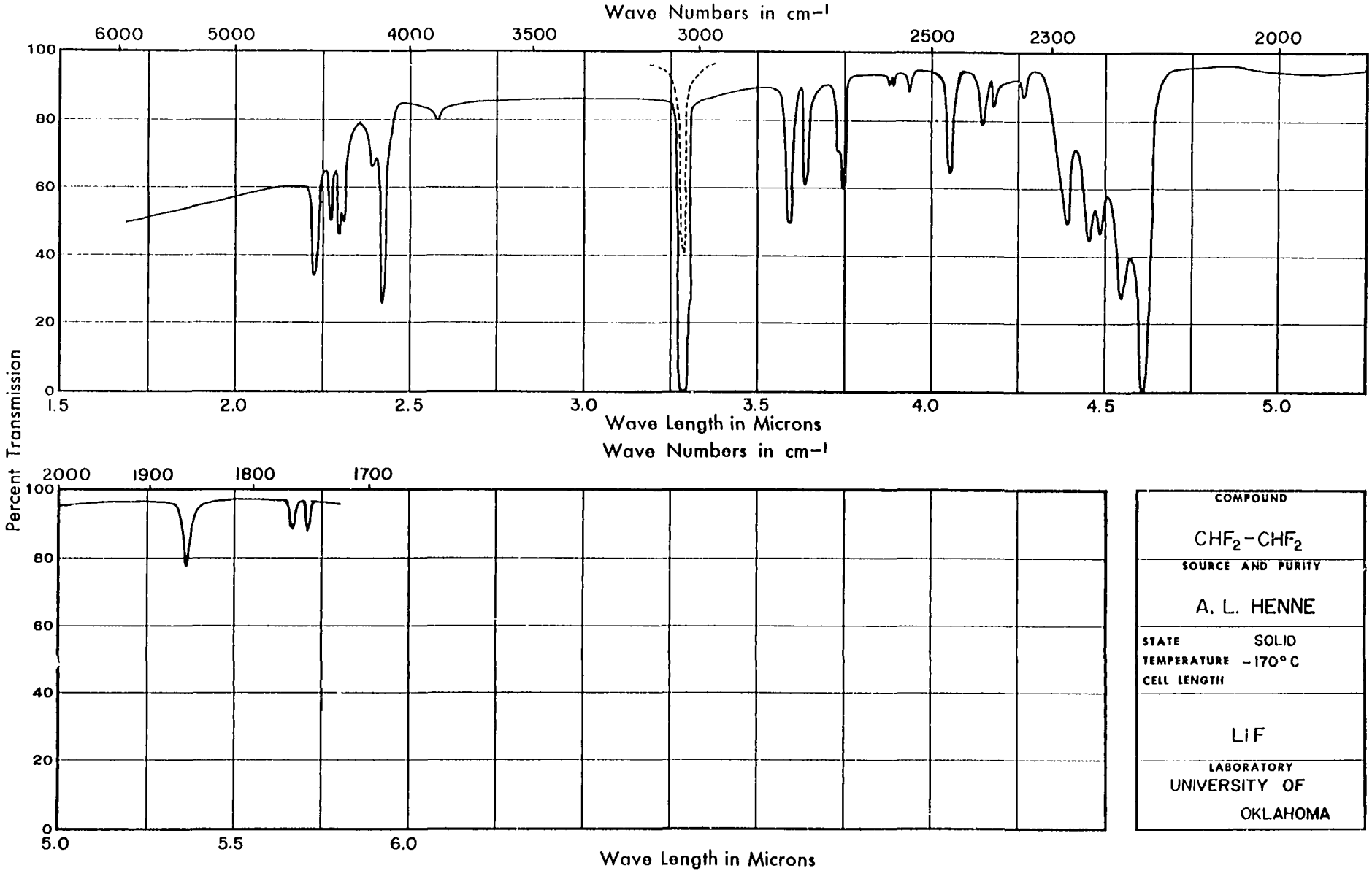

Fig. 11. Infrared Spectrum of Solid CHF_2-CHF_2 (LiF Region)

$6a_g + 4a_u + 3b_g + 5b_u$. Vibrations of species a_u and b_u are active only in the infrared; vibrations of species a_g and b_g are active only in the Raman spectrum. Raman bands of species a_g are polarized; those of species b_g are depolarized.

It is also found, however, that a number of strong infrared and Raman bands coincide. This indicates that the other rotational isomers consist of two enantiomorphic forms of symmetry C_2 obtained from the trans form by rotating one of the CHF_2 groups a certain angle (probably close to 120°) about the C-C bond in either direction. These two gauche forms will have identical vibrational frequencies, and their normal vibrations divide into 10 of species a and 8 of species b. All of them are active in both spectra. Raman bands of species a are polarized; those of species b are depolarized.

These conclusions are strongly supported by the fact that, with a few exceptions which will be discussed below, none of the infrared bands observed in the solid have counterparts in the Raman spectrum. This shows that, as in the case of 1,2-dichloroethane,[20] only the trans form is present in the crystal. The solid formed by slow condensation of the vapor at -170°C appears to be almost completely crystalline. However, when the solid film is formed very fast an appreciable fraction of the material appears to be in an amorphous or glassy state.

Assuming the internuclear distances C-C = 1.54,

C-F = 1.37, C-H = 1.093A, and tetrahedral angles, one finds the following principal moments of inertia for the trans form: 169.4, 274.4 and 420.7 x 10^{-40} gcm^2. The axes of smallest and largest moments of inertia lie in the symmetry plane, the latter making an angle of 64°57' with the C-C bond. Infrared bands of species a_u should, therefore, have type B contours in the spectrum of the gas, while bands of species b_u should have contours that are hybrids of types A and C. Extrapolations from Badger and Zumwalt's curves[39] give a QQ separation of 7 cm^{-1} for type B bands and PR separations of 15 and 18 cm^{-1} for A and C bands, respectively.

With the additional assumption that one end-group is rotated 120° relatively to the other, the principal moments of inertia of the gauche form are found to be 214.9, 315.4 and 338.4 x 10^{-40} gcm^2. The axis of intermediate moment of inertia coincides with the two-fold symmetry axis. Thus, infrared bands of species b should have contours that are hybrids between types A and C. The QQ separation for type B bands should be 3 cm^{-1} and the PR separations for bands of types A and C should be 16 and 19 cm^{-1}, respectively.

On the basis of these criteria, it has been possible to make practically complete assignments of vibrational

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[39]R. M. Badger and L. R. Zumwalt, J. Chem. Phys. 6, 711 (1938).

fundamentals for both trans and gauche isomers. For brevity, the isomer, or isomers, to which a frequency is ascribed will not be stated explicitly in what follows but will be implied by the species assignment, a_g, a_u, b_g and b_u referring to the trans and a and b to the gauche isomer. The very strong band at 2996 cm^{-1}, and the prominent shoulders at 3003 and 2987 cm^{-1}, in the infrared spectrum of the gas must represent the b_u fundamental of the trans isomer and the a and b fundamentals of the gauche isomer associated with C-H stretching. In the Raman spectrum of the liquid the a_g fundamental of the trans isomer and the a and b fundamentals of the gauche overlap to form what appears to be a single broad band with maximum near 3015 cm^{-1}. In the infrared spectrum of the crystalline solid a very strong band is found at 3040 cm^{-1} which is interpreted as the b_u C-H stretching mode of the trans isomer.

In the region from 900 to 1500 cm^{-1} 9 fundamentals are expected for each isomer, their vibrations consisting of C-C stretching, C-F stretching and C-H bending. The fact that fewer than the expected number of bands are found indicates that some of the observed frequencies are common to trans and gauche isomers. For this reason, and because some of the frequency shifts on going from gas to solid are quite large in this region, there is some uncertainty in the assignment of some of these fundamentals.

The broad, polarized Raman band at 1440 cm^{-1}, which

has no observed counterpart in the infrared spectrum, is interpreted as overlapping $\underline{a}_g$ and $\underline{a}$ fundamentals, probably involving mainly C-H bending. The strong, diffuse but polarized, Raman band at 1360 cm^{-1}, to which there corresponds a strong infrared band at 1389 cm^{-1} in the gas but none in the solid, is also interpreted as overlapping $\underline{a}_g$ and $\underline{a}$ fundamentals. The motion is probably largely C-F stretching. The infrared bands at 1336 and 1344 cm^{-1} in gas and solid, respectively, are assigned as a $\underline{b}_u$ fundamental. To the strong infrared band at 1322 cm^{-1} in the gas there appear to correspond a Raman band at 1321 cm^{-1} in the liquid and two infrared bands at 1314 and 1310 cm^{-1} in the crystalline solid. The intensity ratio of the latter two bands varies with the temperature at which crystallization takes place, indicating that they belong to different crystal forms. All of these bands are interpreted as an $\underline{a}_u$ and a $\underline{b}$ fundamentals. The rather low value of the observed depolarization ratio of the Raman band is assumed to be caused by experimental uncertainty. The very strong infrared band at 1302 cm^{-1} in the gas is interpreted as a $\underline{b}$ fundamental, in spite of the facts that no corresponding Raman band was observed and that a weak infrared band was found in the solid at 1292 cm^{-1}. The latter is believed either to be caused by a small amorphous or glassy component of the solid or to be a combination band.

The very strong infrared band at 1207 cm^{-1}, which is

absent in the crystal, and the medium intensity Raman band at 1192 cm^{-1} are interpreted as a b fundamental, and the Raman band is also ascribed to an overlapping b_g fundamental. The strong infrared band at 1147 cm^{-1} in the gas and the strong and apparently polarized Raman band at the same wave number are assigned as an a fundamental.

The very intense infrared band at 1134 cm^{-1} in the gas is shifted to 1109 cm^{-1} in the solid and has no corresponding Raman band. It is interpreted as a b_u fundamental. Although it is not well separated from the band just mentioned, there appears to be a strong infrared band near 1125 cm^{-1} in the gas and at 1089 cm^{-1} in the crystal. A corresponding Raman band is observed at 1094 cm^{-1}. It is assumed that these arise from overlapping a_u and a fundamentals. The weak Raman band observed at 1080 cm^{-1} is assigned as a b_g fundamental, and the strong infrared band at 1073 cm^{-1} is interpreted as a b fundamental. The strong infrared band at 905 cm^{-1} in the gas, which is not present in the crystal, and the strong, polarized band at 901 cm^{-1} in the Raman spectrum are interpreted as overlapping a and a_g fundamentals. They probably involve largely C-C stretching.

The infrared band at 775 cm^{-1} in the gas is absent in the solid but a depolarized Raman band is found at 772 cm^{-1}. These evidently represent a b fundamental. The strong infrared bands at 622 and 594 cm^{-1} are both polarized. The

former has no counterpart in the infrared spectrum, the latter corresponds to a medium intensity infrared band at 598 cm^{-1} found only in the spectrum of the gas. These bands must be interpreted as an $\underline{a_g}$ and an $\underline{a}$ fundamental, respectively. The infrared band at 539 cm^{-1} in the gas has definitely a PQR structure with PR separation 15 cm^{-1}. A corresponding band is found at 537 cm^{-1} in the spectrum of the solid but none is observed in the Raman spectrum. These bands are assigned as a $\underline{b_u}$ fundamental. The motions associated with the four last-mentioned fundamentals can probably best be described as deformations of the CF_2H groups.

Overlapping the $\underline{b_u}$ fundamental at 539 cm^{-1}, a rather strong infrared band, of uncertain contour, appears near 522 cm^{-1} in the spectrum of the gas, but no indication of such a band is observed in the solid. A medium intensity Raman band occurs at 522 cm^{-1}. These bands are assigned as a $\underline{b}$ fundamental. The depolarized Raman band at 478 cm^{-1}, which has no counterpart in the infrared spectrum, is assigned as a $\underline{b_g}$ fundamental.

In a wide region around 425 cm^{-1} the infrared absorption by the gas is extremely strong but very complex, indicating the presence of more than one fundamental. In the infrared spectrum of the solid there is a single strong band with maximum at 417 cm^{-1}. However, when the sample was solidified very rapidly, presumably forming a mixture of crystalline aggregate and glass, a second, weaker band was

observed at 408 cm^{-1}. In the Raman spectrum a medium intensity, slightly polarized band is found at 413 cm^{-1}. The latter is interpreted as an a fundamental and the infrared band in the crystalline solid is assigned as an a_u fundamental. The wave numbers for these fundamentals in the gas cannot be given accurately but are assumed to be 419 and 430 cm^{-1}, respectively.

A strong infrared band is observed at 393 cm^{-1} in the gas but not in the solid. Although no corresponding Raman band was found, it is assigned as an a fundamental. The strong, polarized Raman band at 361 cm^{-1} has no infrared counterpart and is therefore assigned as an a_g fundamental. The weak Raman band at 188 cm^{-1} is interpreted as a b fundamental. The vibrations associated with the fundamentals mentioned having wave numbers 522 cm^{-1} or lower may be roughly characterized as rocking motions.

There remain the lowest a fundamental of the gauche isomer and the two lowest fundamentals of the trans isomer. The a fundamental, involving largely twisting, may be represented by a weak and somewhat uncertain Raman band at 130 cm^{-1}. The two fundamentals of the trans isomer, of species b_u (rocking) and a_u (twisting) lie outside the range of the CsBr prism and are inactive in the Raman spectrum. There is some evidence from combination bands that they lie near 220 and 130 cm^{-1}, respectively, but this is quite uncertain.

The assigned fundamentals are listed in Tables III and IV. The validity of these assignments may be tested by the sum rule derived by Mizushima et al.[40] For the gauche isomer $\sum_i \nu_i^2 = 33.02 \times 10^6$. Taking the uncertain values mentioned above for the two lowest fundamentals, one finds 32.74×10^6 for the corresponding sum for the trans isomer. The difference is less than 0.9%. The lower value found for the trans isomer may result from the fact that half of the fundamental vibrational frequencies for this isomer are obtained from the Raman spectrum of the liquid phase. The empirical sum rule of Bernstein and Pullin[41] is also quite well satisfied, the sums being $\sum_i \nu_i = 19{,}940$ for the gauche and $\sum_i \nu_i = 19{,}690$ for the trans isomer.

In terms of the assigned fundamentals it has been possible to assign all of the observed Raman bands and practically all of the infrared bands. However, because of the large dependence of many of the frequencies upon the state of aggregation, the correlation of several bands in the three spectra is very difficult, and their interpretations are therefore somewhat uncertain. Most, if not all, of the very weak bands that have been left uninterpreted can be explained as ternary combination bands. However, in view of the large number of fundamentals such interpretations

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[40]Mizushima, Shimanouchi, Nakagawa, and Miyake, J. Chem. Phys. 21, 215 (1953).

[41]H. J. Bernstein and A. D. A. Pullin, J. Chem. Phys. 21, 2188 (1953).

are in most cases not unique and have therefore not been included in Table II.

The Enthalpy Difference Between the Rotational Isomers

As the CHF_2 - CHF_2 gas was heated from 30° to 170°C the infrared bands assigned to the gauche isomer increased in intensity, while those assigned to the trans form became weaker, showing that the latter is the more stable. For the purpose of determining the enthalpy difference the peak extinctions of the following bands were measured at 30°, 70°, 110°, 140°, and 170°C: trans: 1134, 1322, and 539 cm^{-1}, gauche: 1207, 775, and 598 cm^{-1}, and the graphical method of Bernstein[42] was used. The following result was obtained: $\Delta H^{o} = 1160 \pm 100$ cal/mole. Because of the uncertainty in several of the fundamental vibrational frequencies, especially the two lowest frequencies for the trans isomer, the energy difference ΔE_{o}^{o} was not calculated.

The three identical Raman exposures, at 25°, -25° and -70°C, did not reveal any appreciable intensity variations with temperature, indicating that ΔH^{o} is much smaller, probably less than 400 cal/mole, for the liquid state. This can be explained only in part by Onsager's theory of dielectrics,[43] according to which a spherical molecule of dipole moment μ and radius a loses the potential energy

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[42] H. J. Bernstein, J. Chem. Phys. 18, 897 (1950).

[43] L. Onsager, J. Am. Chem. Soc. 58, 1486 (1936).

$E_r = (\varepsilon - 1)\mu^2/(2\varepsilon + 1)a^3$ when transferred from vacuum ($\varepsilon = 1$) to a medium of dielectric constant ε. Using the bond moments $\mu_{C-H} = 0.4$, $\mu_{C-F} = 1.45$ debyes,[18] one finds by simple vector addition the values 1.73 D for the gauche and 0 for the trans isomer. The dielectric constant of liquid $CHF_2 - CHF_2$ is not known. However, since the formula is not very sensitive to changes in ε, it is probably a fairly good approximation to put $\varepsilon = 10$, which is the value given for 1,2-dichloroethane.[44] Taking a = 1.6A, one finds E_r (gauche) = 320 cal/mole, E_r (trans) = 0. While this is of the right order of magnitude it is considerably smaller than the observed change in ΔH^o.

Discussion

It is of interest to compare the results found here with those previously reported for $CHCl_2 - CHCl_2$ and $CHBr_2 - CHBr_2$. In the case of both of these compounds the gauche isomer is the more stable in the liquid state,[45] the enthalpy differences being 1100 and 910 cal/mole, respectively. $CHCl_2 - CHCl_2$ crystallizes in the gauche form, while $CHBr_2 - CHBr_2$ crystallizes as trans or gauche according to the experimental conditions.[45] For gaseous $CHCl_2 - CHCl_2$ ΔH^o is very small.[20,46] No information is available about

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[44] P. Walden: Z. physik. Chem. 70, 596 (1909).

[45] R. E. Kagarise, J. Chem. Phys. 24, 300 (1956).

[46] J. R. Thomas and W. D. Gwinn, J. Am. Chem. Soc. 71, 2785 (1949).

gaseous $CHBr_2$ - $CHBr_2$.

It is rather difficult to understand why CHF_2 - CHF_2 behaves differently from the two other compounds. If, as claimed by Mizushima,[47] steric hindrance is the most important factor in determining the relative stability of the rotational isomers of halogenated ethanes, one would expect $CHCl_2$ - $CHCl_2$ and $CHBr_2$ - $CHBr_2$ to have a greater rather than a smaller probability of existing in the trans form than CHF_2 - CHF_2. The stabilization of the trans form of this compound may be a result of intramolecular hydrogen bonding which should be nearly twice as strong in the trans as in the gauche form.

A normal coordinate treatment of the trans form of this molecule using Wilson's F and G matrix method,[48,49] has been started. The G-matrix elements of species a_g, a_u, b_g and b_u have been calculated. Tentative calculations have been completed for the corresponding F matrices, using force constants derived by Cleveland, Meister et al., for $CHCl_2$ - $CHCl_2$[31] and fluorinated halomethanes.[11] A preliminary calculation of the fundamental frequencies of species b_g gave the values 336, 1014 and 1409 cm^{-1} compared to the

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[47] Reference 20, page 68.

[48] E. B. Wilson, Jr., J. Chem. Phys. 7, 1047 (1939); 9, 76 (1941).

[49] E. B. Wilson, Jr., J. C. Decius and P. C. Cross, Molecular Vibrations (McGraw-Hill Book Company, Inc., New York, 1955).

experimental values 478, 1080 and 1192 cm^{-1}, respectively. A change of the force constants with trial and error is evidently necessary to obtain a good agreement between the calculated and experimental fundamental frequencies. The normal coordinate work of CHF_2 - CHF_2 is being continued by Mr. S. Quiros-Guardia using an IBM 650 electronic computer.

TABLE I

INFRARED SPECTRAL DATA FOR GASEOUS AND SOLID CHF_2 - CHF_2

Gas		Solid[a]		
Wave Number	Description[b]	Wave Number	Description[b]	Interpretation[c]
380	m			2 x 188 = 376 A
393	s			a fundamental
413	vs			
419	vs	408[d]		a fundamental
423	vs			
425	vs			
430	vs	417	s	a_u fundamental
434	s			
501	vvw			
515	m			130 + 393 = 523 A
522	s			b fundamental
531	s			
539	vs	537	s	b_u fundamental
546	s			
598	m			a fundamental
685	w			
692	w			188 + 522 = 710 A
698	w			
772	vs			
775	vs			b fundamental
779	vs			

TABLE I--Continued

Gas		Solid[a]		
Wave Number	Description[b]	Wave Number	Description[b]	Interpretation[c]
785	m			188 + 598 = 786 B; 361 + 430 = 791 B_u
831	w			
840	w	834	m	2 x 419 = 838 A; [220] + 622 = 842 B_u
845	w			
893	w			361 + 539 = 900 B_u; [130] + 775 = 905 B
905	s			a fundamental
911	w			
918	vw			393 + 522 = 915 B
1013	vw			419 + 598 = 1017 A
1029	m	1021	vw	[130] + 905 = 1035 A_u
1061	w	1062	vw	430 + 622 = 1052 A_u
1073	s			b fundamental
1125	s	1089	vs	a_u + a fundamentals
1134	vs	1109	vs	b_u fundamental
1147	s			a fundamental
		1161	vw	539 + 622 = 1161 B_u
1196	s	1192[d]	vw	[130] + 1080 = 1210 B_u
1207	vs			b fundamental
1214	s			
1265	vw	1263	w	188 + 1073 = 1261 A

TABLE I--Continued

Gas		Solid[a]		
Wave Number	Description[b]	Wave Number	Description[b]	Interpretation[c]
1276	w			[130] + 1147 = 1277 A
1302	vs	1292	w	b fundamental; [220] + 1080 = 1300 A_u
		1310	vs	
1322	vs			a_u + b fundamentals
		1314	vs	
1336	vs	1344	vs	b_u fundamental
1362	vw	1363	vw	598 + 775 = 1373 B
1389	s			a fundamental
1499	m			598 + 905 = 1503 A
		1579	vw	[220] + 1360 = 1580 B_u
1603	m	1599	vw	478 + 1125 = 1603 B_u
		1716	vvw	539 + 1192 = 1731 A_u
1754	m	1751	vvw	622 + 1134 = 1756 B_u
1769	w			393 + 1389 = 1782 A
1855	vw	1864	vw	430 + 1440 = 1870 A_u; 419 + 1440 = 1859 A
2109	vw			905 + 1207 = 2112 B
2228	s	2169	s	905 + 1322 = 2227 A_u; 1080 + 1134 = 2214 A_u
2254	m	2198	m	905 + 1336 = 2241 B_u; 2 x 1125 = 2250 A
		2232	w	
2278	m	2244	w	1125 + 1147 = 2272 A ?

TABLE I--Continued

Gas		Solid[a]		
Wave Number	Description[b]	Wave Number	Description[b]	Interpretation[c]
2291	m	2276	w	1125 + 1192 = 2317 B_u; 2 x 1147 = 2294 A; 905 + 1389 = 2294 A
		2345	vw	1192 + 1134 = 2326 A_u; 905 + 1440 = 2345 A ?
		2390	vw	1080 + 1322 = 2402 B_u
2407	vw	2410	vw	1080 + 1336 = 2416 A_u
2441	w			1147 + 1302 = 2449 B
2453	w			1073 + 1389 = 2462 B
2460	w	2461	w	1125 + 1360 = 2485 A_u
2491	vw			1207 + 1302 = 2509 A
2573	m	2541	w	1134 + 1440 = 2574 A_u
2590	vw			1207 + 1389 = 2596 B; 2 x 1302 = 2604 A
2664	w	2672	m	1322 + 1360 = 2682 A_u
2672	w	2681	w	1336 + 1360 = 2696 B_u
2739	w	2748	m	1322 + 1440 = 2762 A_u; 1302 + 1440 = 2742 B
2775	w	2780	m	1336 + 1440 = 2776 B_u; 2 x 1389 = 2778 A
2807	vw			1389 + 1440 = 2829 A
2845	vw			2 x 1440 = 2480 A
2916	vw			
2987	vs			
2996	vs	3040	vs	a + b + b_u fundamentals

TABLE I--Continued

Gas		Solid[a]		
Wave Number	Description[b]	Wave Number	Description[b]	Interpretation[c]
3003	vs			
3067	vvw			
3319	vw			393 + 3000 = 3393 A + B
3405	vw			419 + 3000 = 3419 A + B
3738	vvw			775 + 3000 = 3775 A + B
3834	vvw			905 + 3000 = 3905 A + B
4100	m	4129	m	1125 + 3015 = 4140 A_u + A + B
4134	w	4184	vw	1134 + 3015 = 4149 B_u; 1147 + 3000 = 4147 A + B
		4333	w	1322 + 3015 = 4337 A_u
4297	w	4354	w	1336 + 3015 = 4351 B_u
		4390	w	1360 + 3000 = 4360 B_u
4440	m	4480	w	1440 + 3000 = 4440 B_u

[a]Solid film at -170°C. The thickness varied from record to record, but was not measured. Hence, the relative intensities indicated have less significance than for the gas.

[b]The following abbreviations have been used: s strong, m medium, w weak, and v very.

[c]The species a_u and b_u refer to the trans isomer, the species a and b to the gauche isomers. Wave numbers in brackets are inferred from combination bands.

[d]This band was observed only when the solid film was deposited very rapidly. It is believed to belong to an amorphous or glassy state.

TABLE II

RAMAN SPECTRAL DATA FOR LIQUID CHF_2 - CHF_2

Wave Number	Description[a]	Exciting Hg lines[b]	Interpretation[c]
ca 130	vw	e	a fundamental
188	w	e	b fundamental
361	s,sh (0.4)	±e,k	a_g fundamental
413	m (0.8)	±e,k	a fundamental
478	m (dp)	e	b_g fundamental
522	m (dp)	e	b fundamental
578	vw	e	188 + 393 = 581 B
594	s,sh (0.2)	±e,k,i	a fundamental
622	vs,sh (0.2)	±e,k,i	a_g fundamental
772	m,d (0.8)	e,k	b fundamental
837	w	e	2 x 413 = 826 A; 2 x ca 420 = ca 840 A_g
901	s (0.3)	e,k,i	a + a_g fundamentals
1080	w	e	b_g fundamental
1094	vs (0.3)	e,k	a fundamental
1147	s (0.6)	e,k	a fundamental
1192	m (dp)	e,k	b + b_g fundamentals
1247	vw	e	130 + 1125 = 1255 A; 361 + 901 = 1262 A_g
1321	m (0.7)	e	b fundamental
1360	s (0.3)	e,k	a + a_g fundamentals
1440	m,b (0.3)	e	a + a_g fundamentals
3010-3025	vs (0.2)	e,k,i	a + a_g + b fundamentals

[a]The following abbreviations have been used: s strong, m medium, w weak, v very, d diffuse, sh sharp, dp depolarized, b broad. The numbers in parentheses are measured depolarization ratios.

[b]The meanings of the Kohlrausch symbols are: e 4358A, k 4047A, i 4078A; ± indicates that the Raman band has been observed both as a Stokes and an anti-Stokes shift.

[c]Fundamentals of species a_g and b_g refer to the trans isomer, those of species a and b to the gauche isomers.

TABLE III

FUNDAMENTAL VIBRATIONAL FREQUENCIES
OF trans CHF_2 - CHF_2 (in cm^{-1})[a]

Species	Infrared		Raman	Approximate Motion
	Gas	Solid	Liquid	
a_g			ca 3015 vs	CH stretch
a_g			1440 m,b (0.3)	CH bending
a_g			1360 s (0.3)	CF stretch
a_g			901 s (0.3)	CC stretch
a_g			622 vs (0.2)	CHF_2 deform
a_g			361 s (0.4)	Rocking
a_u	1322 s	1314 (1310) vs		CH bending
a_u	1125 vs	1089 s		CF stretch
a_u	ca 430 s	417 vs		Rocking
a_u	[130][b]	[130][b]		Twisting
b_g			1192 m (dp)	CH bending
b_g			1080 w	CF stretch
b_g			478 m (dp)	Rocking
b_u	ca 3000 vs	3040 vs		CH stretch
b_u	1336 s	1344 s		CF stretch
b_u	1134 vs	1109 s		CH bending
b_u	539 s	537 s		CHF_2 deform
b_u	[220][b]	[220][b]		Rocking

[a]See footnotes to Tables I and II for the explanation of the abbreviations used.

[b]Wave numbers in brackets are inferred from combination bands.

TABLE IV

FUNDAMENTAL VIBRATIONAL FREQUENCIES OF *gauche* CHF_2 - CHF_2 (in cm^{-1})[a]

Species	Infrared Gas	Raman Liquid	Approximate Motion
a	ca 3000 vs	ca 3015 vs,b	CH stretch
a	--	1440 m,b (0.3)	CH bending
a	1389 s	1360 s (0.3)	CF stretch
a	1147 s	1147 s (0.6)	CH bending
a	1125 s	1094 vs (0.3)	CF stretch
a	905 s	901 s (0.3)	CC stretch
a	598 m	594 s (0.2)	CHF_2 deform
a	ca 419 vs	413 m (0.8)	Rocking
a	393 s	--	Rocking
a		ca 130 vw	Twisting
b	ca 3000 vs	ca 3015 vs,b	CH stretch
b	1322 s	1321 m (0.7)	CF stretch
b	1302 vs	--	CH bending
b	1207 vs	1192 m (dp)	CH bending
b	1073 s	--	CF stretch
b	775 vs	772 m,d (0.8)	CHF_2 deform
b	522 m	522 m (dp)	Rocking
b	--	188 w	Rocking

[a]For abbreviations used, see footnotes to Tables I and II.

CHAPTER IV

INFRARED AND RAMAN SPECTRA OF $CH_2F - CH_2F$

Introduction

The vibrational spectra of a number of fluorinated ethanes having asymmetrical end-groups have been studied with special reference to rotational isomerism.[28,29] It is of special interest to compare the spectra of $CH_2F - CH_2F$ with those of $CH_2Cl - CH_2Cl$ and $CH_2Br - CH_2Br$ which have been studied in great detail, particularly by Mizushima and co-workers.[20]

In the present chapter infrared and Raman spectral data are reported for $CH_2F - CH_2F$ and the rotational isomerism exhibited by this compound is studied. A tentative assignment of all vibrational fundamentals for the gauche form, and all but the lowest fundamental for the trans form, has been carried out, and the spectra have been interpreted in detail.

Experimental Results

The synthesis of $CH_2F - CH_2F$ in low yield by treating $CH_2Br - CH_2Br$ with HgF_2 has been reported by Henne and Renoll.[50]

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[50] A. L. Henne and M. W. Renoll, J. Am. Chem. Soc. 58, 889 (1936).

The sample was unstable, however, and exploded after 10 days. A synthesis of the compound (bp 30.7°C at 760 mm) has more recently been carried out by Edgell and Parts[51] from p-toluene sulfonic acid ester. The present sample (bp 31°C at 750 mm) was prepared by Dr. L. H. Beck in the laboratory of Professor A. L. Henne at Ohio State University following essentially Edgell's procedure.

A gas chromatogram showed the sample to contain less than 0.5% of more volatile impurities. A vapor density measurement at 28°C gave the molecular weight of 65.2, which agrees quite well with the theoretical value 66.05. No explosion has occurred. No abnormal pressure in the sealed Raman tubes has been observed, nor any decomposition of the gas when heated to 180°C.

The infrared absorption spectrum of the gas at room temperature was recorded with the aid of a Perkin-Elmer Model 112 spectrometer equipped with CsBr, NaCl and LiF prisms and 6-cm and 10-cm and 1-m cells. To study the rotational isomerism, the infrared spectrum of the gas in an electrically heated 10-cm cell, was obtained also at 70°, 110°, 140° and 170°C. The infrared spectrum of the pure liquid was obtained in sealed cells of thickness 0.0267 and 0.1043 mm. The spectral region from 800 - 120 cm^{-1} was studied with the sample dissolved in different solvents,

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[51] W. F. Edgell and L. Parts, J. Am. Chem. Soc., 77, 4899 (1955).

ranging from the non-polar carbon tetrachloride to the strongly polar nitromethane. Moreover, the infrared spectrum of the solid at -180°C was recorded by means of a low-temperature cell somewhat similar to that described by Lord et al.[33] The Raman spectrum of the liquid in a sealed Raman tube at 35°C and -25°C was photographed with an Applied Research Laboratories 3-prism glass spectrograph of reciprocal linear dispersion 15A/mm at 4358A. Polarization measurements were made by the method of Crawford and Horwitz.[36] The infrared spectra are shown in Figs. 12-18, and the wave numbers of the observed absorption maxima (or "shoulders") are listed in Table V. The Raman spectral data are presented in Table VI.

Interpretation

One would expect the configuration of $CH_2F - CH_2F$ to be very similar to those of $CH_2Cl - CH_2Cl$ and $CH_2Br - CH_2Br$.[20] Accordingly, one would expect $CH_2F - CH_2F$ to exist as an equilibrium mixture of trans and gauche isomers in the gaseous and liquid states and as a single rotational isomer in the crystalline state. However, $CH_2F - CH_2F$ seems to behave differently, and its spectra are more difficult to interpret than the spectra of the corresponding chlorine and bromine compounds. In the first place, none of the strong infrared bands present in the gaseous or liquid states disappear in the solid state at -180°C. Thus, both isomers are evidently present in the solid state. A similar situation has been

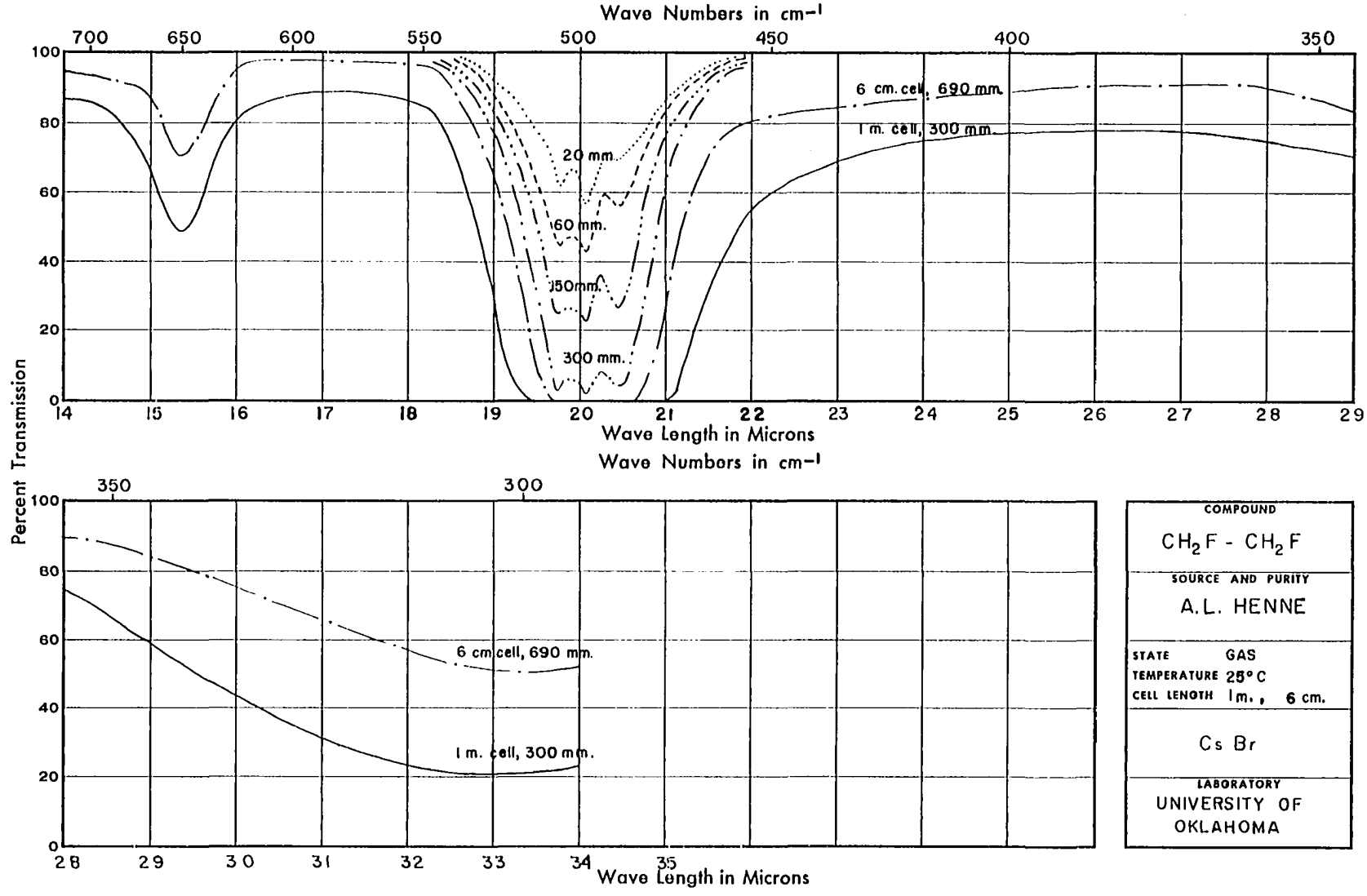

Fig. 12. Infrared Spectrum of Gaseous CH_2F-CH_2F (CsBr Region)

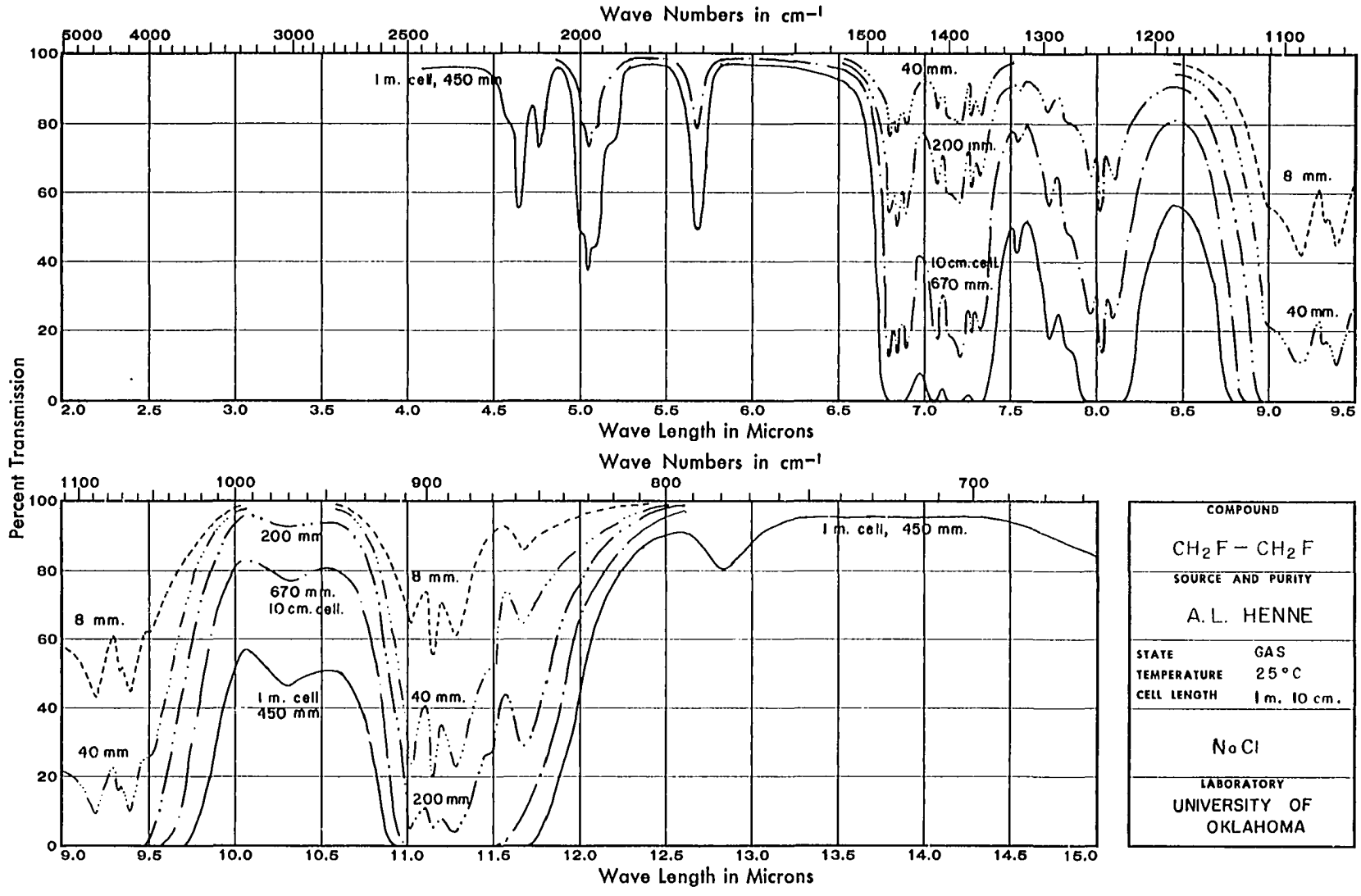

Fig. 13. Infrared Spectrum of Gaseous CH_2F-CH_2F (NaCl Region)

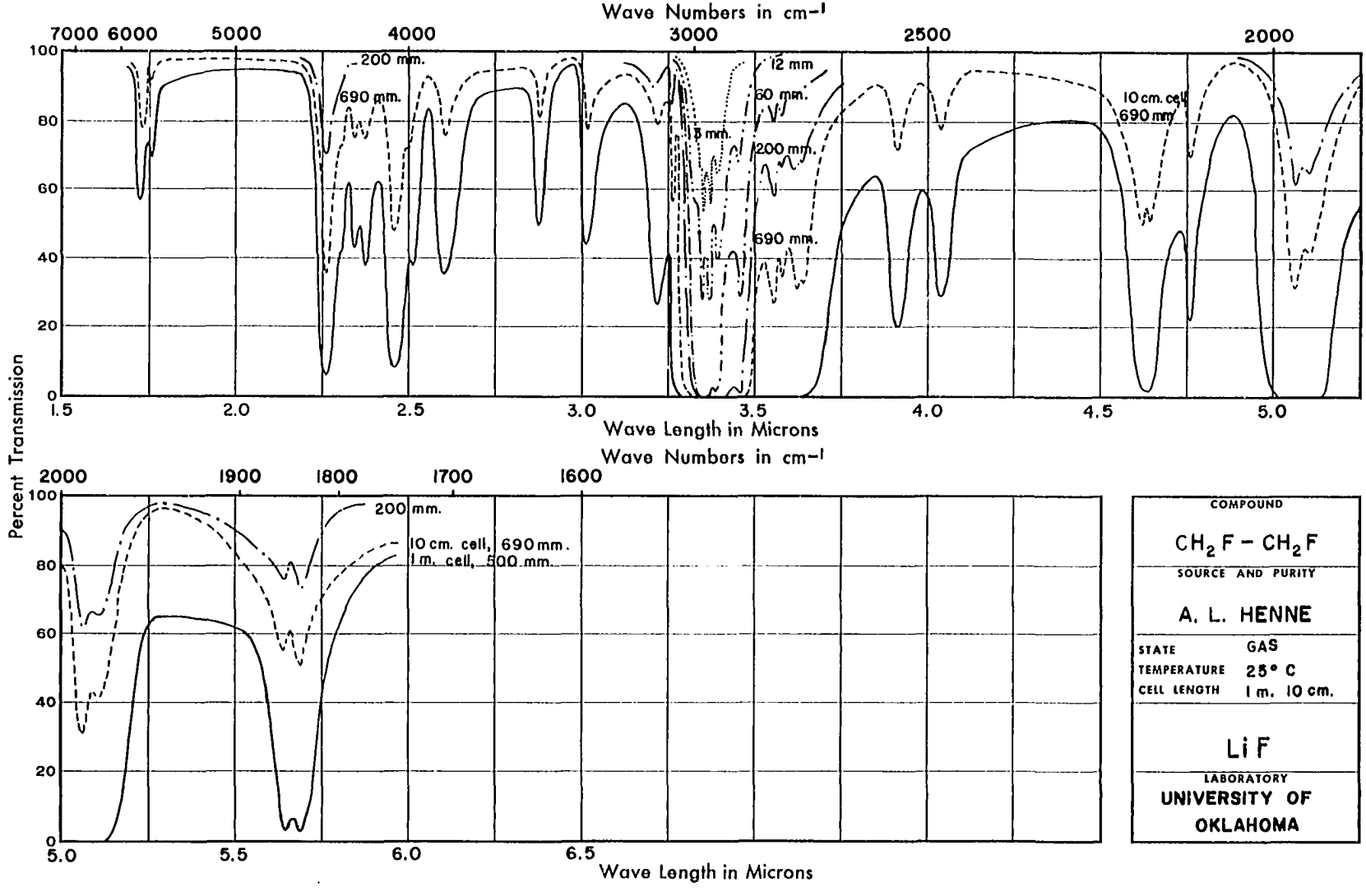

Fig. 14. Infrared Spectrum of Gaseous CH_2F-CH_2F (LiF Region)

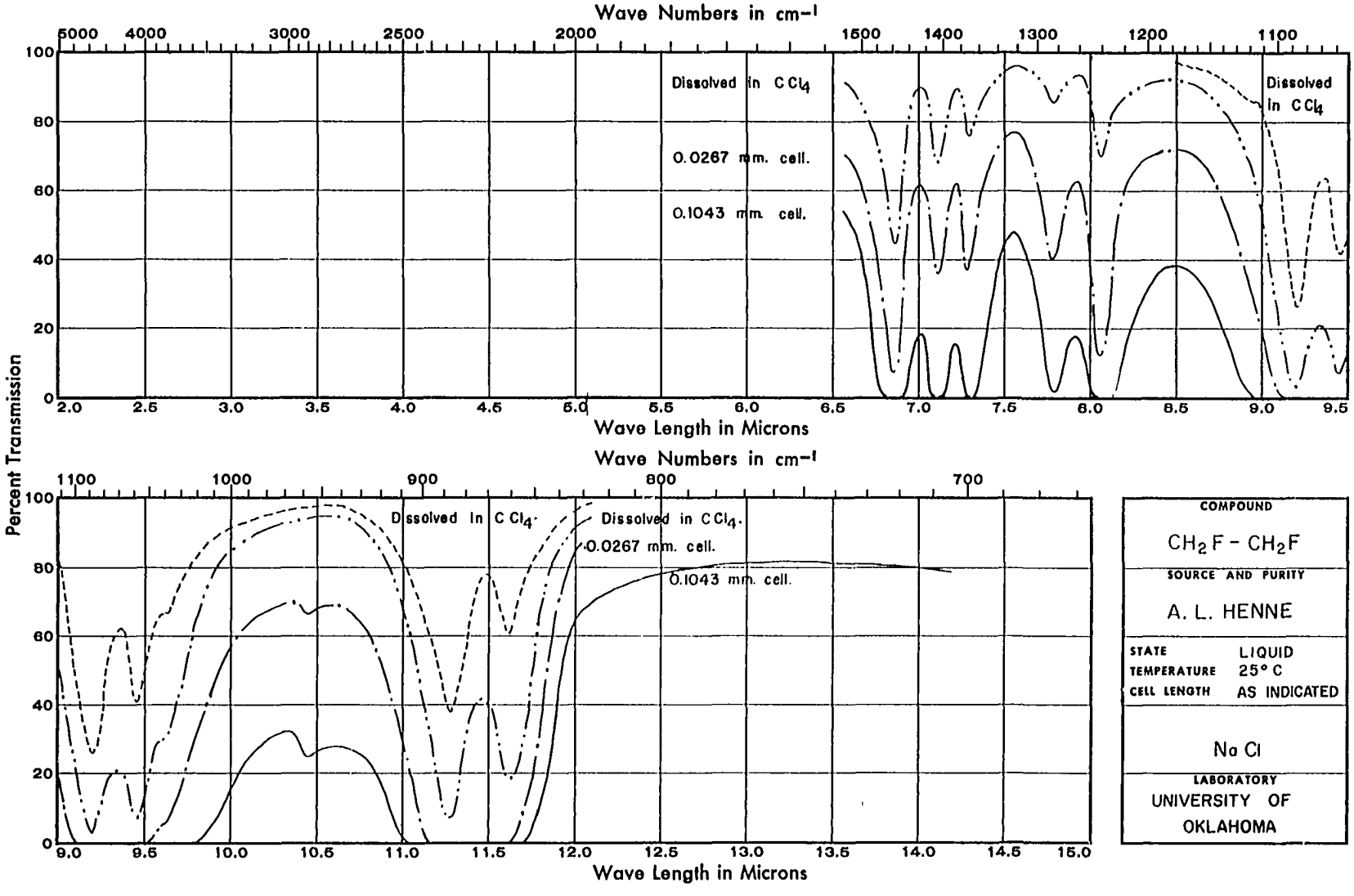

Fig. 15. Infrared Spectrum of Liquid CH_2F-CH_2F (NaCl Region)

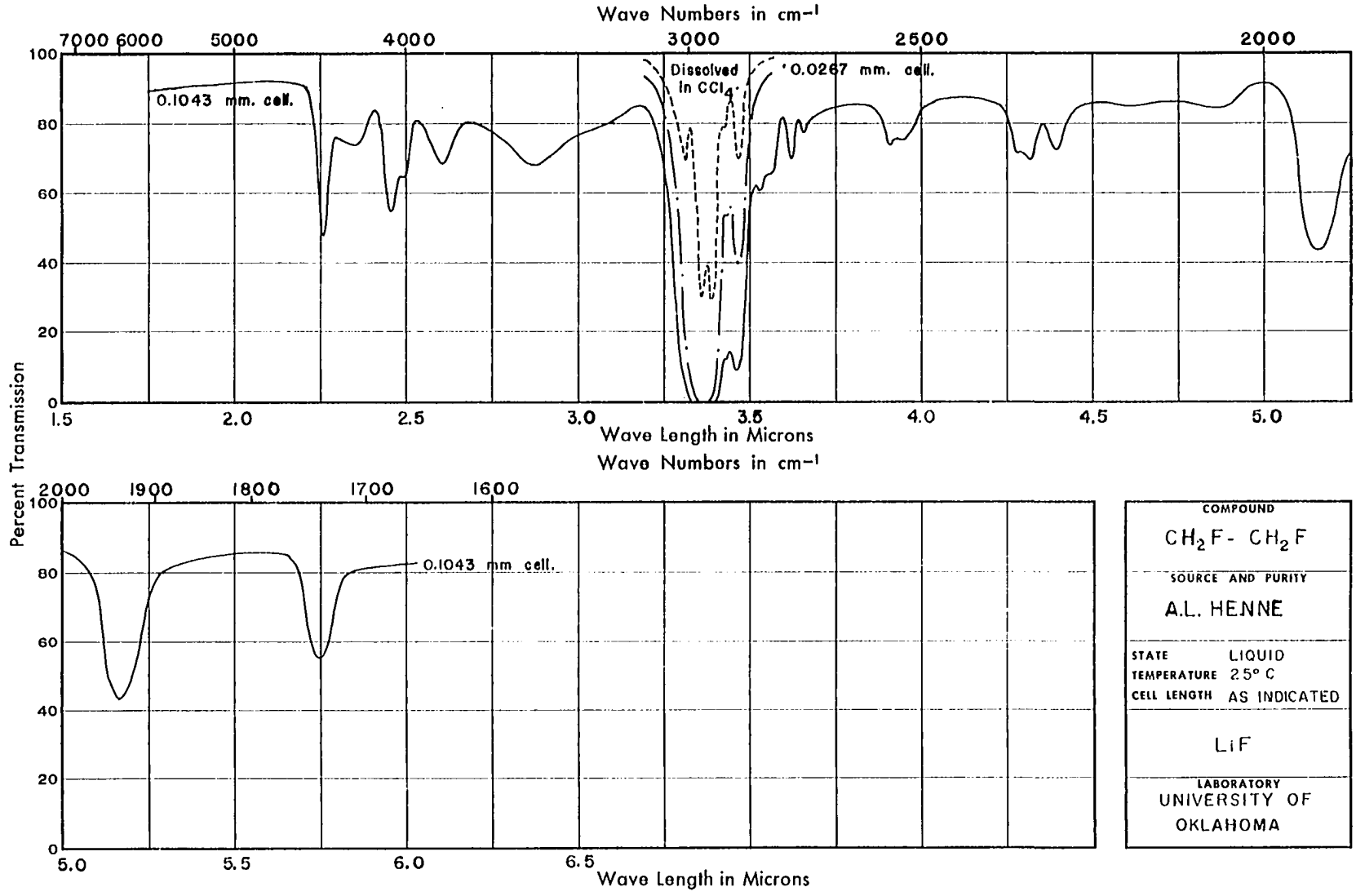

Fig. 16. Infrared Spectrum of Liquid CH_2F-CH_2F (LiF Region)

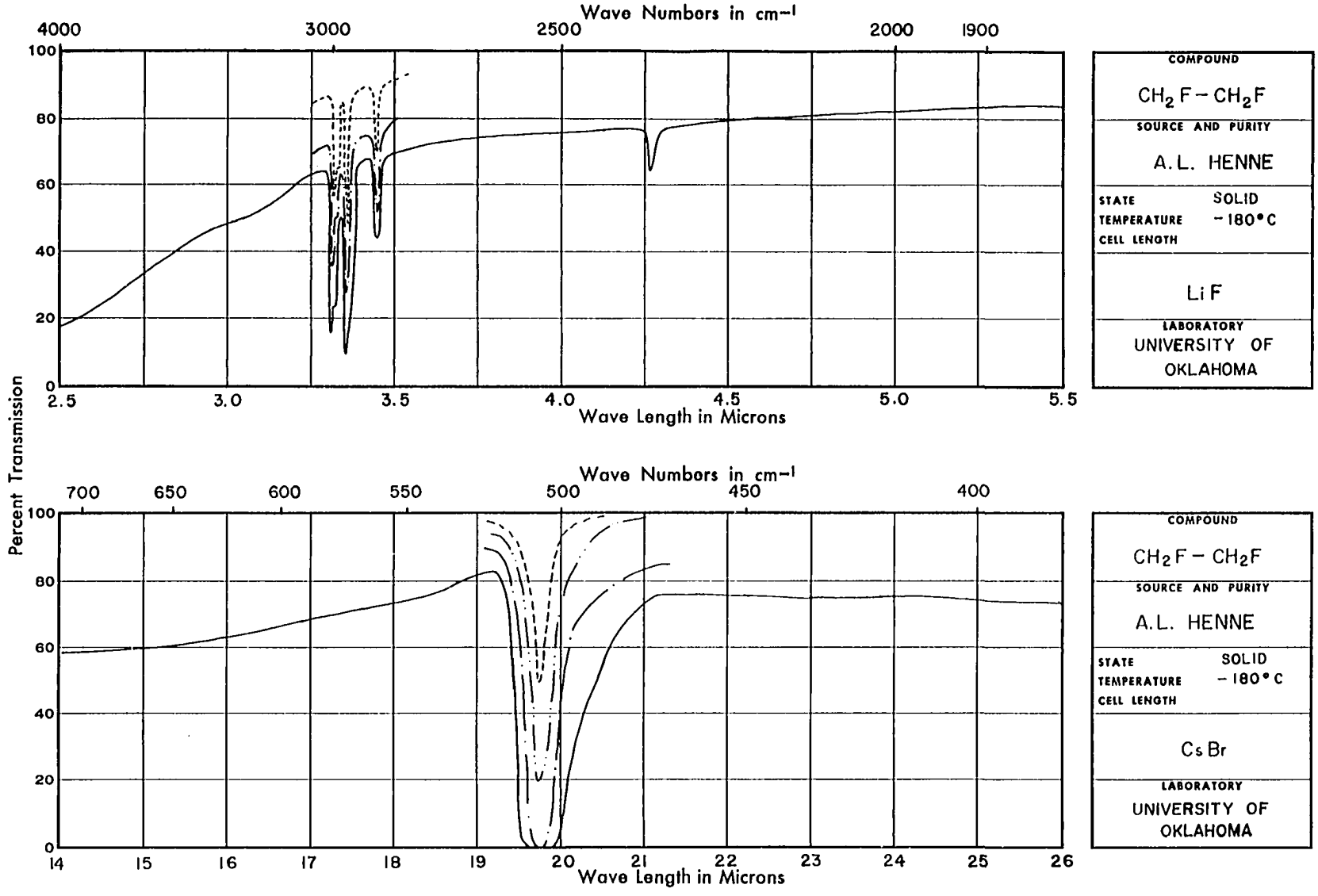

Fig. 17. Infrared Spectrum of Solid CH_2F-CH_2F (CsBr and LiF Region)

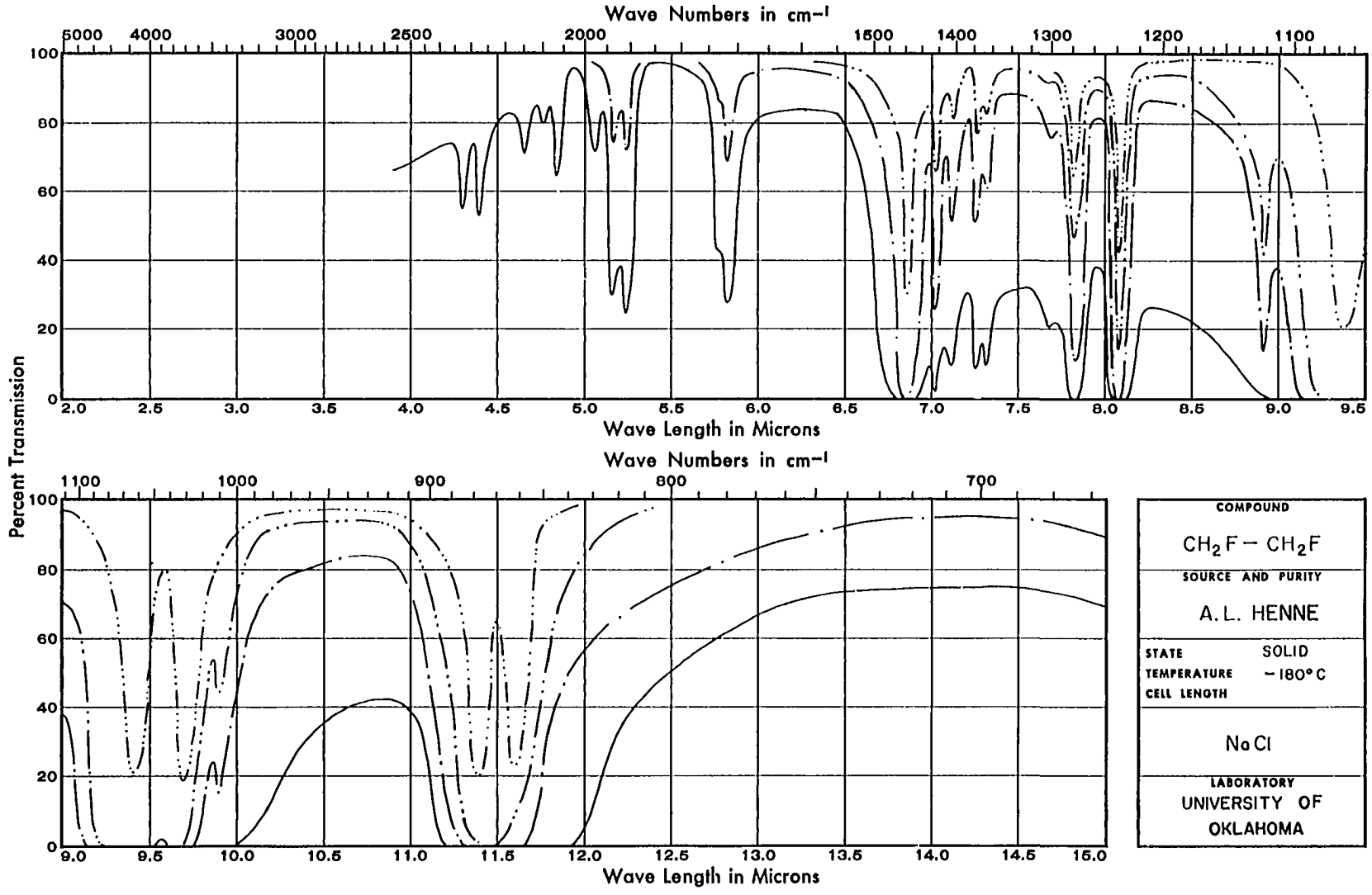

Fig. 18. Infrared Spectrum of Solid CH_2F-CH_2F (NaCl Region)

reported by Kagarise and Daasch for $CFCl_2$ - $CFCl_2$.[29] It is uncertain whether the existence of both isomers in the solid state must be interpreted as a simultaneous crystallization, or if the solid obtained is not crystalline but merely a glassy or amorphous material. The possibility of getting a supercooled liquid instead of a crystalline material has been reported by Malherbe and Bernstein[52] and others.

However, the large frequency and intensity differences observed in many cases between corresponding bands in liquid and solid CH_2F - CH_2F indicate that the solid is crystalline.

Secondly, even if the spectra are too rich in bands to be explained by the existence of one isomer only, the spectra are less rich than the spectra of the corresponding chlorine and bromine compounds. It is therefore necessary to assume that a fairly large number of bands belonging to the different isomers overlap.

Thirdly, the existence of a trans isomer having symmetry C_{2h} should reveal itself by bands occurring in the infrared spectrum but not in the Raman spectrum, and vice versa. This mutual exclusion of infrared and Raman activities was observed for CH_2Cl - CH_2Cl and CH_2Br - CH_2Br and for all other molecules of the form CX_2Y - CX_2Y investigated.[27,29,31,53] The infrared and Raman spectra of the

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[52]F. E. Malherbe and H. J. Bernstein, J. Chem. Phys. 19, 1607 (1951).

[53]R. E. Kagarise and D. H. Rank, Trans. Faraday Soc., 48, 394 (1952).

present molecule, however, show only a few clear-cut instances where strong infrared bands have no counterpart in the Raman spectrum or *vice versa*. Prominent instances are the infrared band at 1376 cm^{-1} and the Raman bands at 450 and 804 cm^{-1}. A number of other cases are questionable.

In spite of these uncertainties, there seems to be sufficiently strong reasons for assuming that $CH_2F - CH_2F$ exists as a mixture of *trans* and *gauche* isomers. Thus, a systematic intensity variation of certain infrared bands is observed when the sample is dissolved in solvents of different polarity. Furthermore, the temperature variations of the intensities of certain Raman bands recorded at 35°C and -25°C support this assumption.

The normal vibrations of the *trans* form of symmetry C_{2h} divide into symmetry species in the following manner: $6a_g + 4a_u + 3b_g + 5b_u$. Vibrations of species a_u and b_u are active only in the infrared; vibrations of species a_g and b_g are active only in the Raman spectrum. Raman bands of species a_g are polarized, those of species b_g are depolarized.

The other isomer will consist of two enantiomorphic forms of symmetry C_2 obtained from the *trans* form by rotating one of the CH_2F groups a certain angle about the C-C bond in either direction. The value of this angle will not affect the symmetry. Because of the electrostatic repulsion between the electronegative fluorine atoms and the attraction between fluorine and hydrogen, the angle will probably be less than

120°. On the other hand, because of the smaller radius of the fluorine atom, steric effects should be less important than in the corresponding chlorine and bromine compounds.

The two gauche forms will have identical vibrational frequencies. Their normal vibrations divide into 10 of species a and 8 of species b. All of them are active in both spectra. Raman bands of species a are polarized; those of species b are depolarized.

Assuming the internuclear distances C-C = 1.54, C-F = 1.37, C-H = 1.093A, and tetrahedral angles, one finds the following principal moments of inertia for the trans form: 30.9, 214.0, 234.2 x 10^{-40} gcm^2. The axis of largest moment is at right angle to the symmetry plane, and the axis of smallest moment makes an angle of 41°51' with the C-C bond. Extrapolation from Badger and Zumwalt's curves[39] is not feasible because of the extreme form of the ellipsoid of inertia. Since the molecule is nearly a symmetrical top, however, the curves given by Gerhard and Dennison[54] may be applied to estimate the contours of the infrared bands. They give a PR separation of 16 cm^{-1} for parallel bands and an intensity of the zero branch equal to 0.12 of the intensity of the entire band. The perpendicular bands, on the other hand, should show no marked rotational branches, the zero branch completely dominating the contour. The a_u bands

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[54]S. L. Gerhard and D. M. Dennison, Phys. Rev. 43, 197 (1933).

are perpendicular. The b_u bands are hybrids.

Because the exact configuration of the gauche form is unknown, a calculation of the moments of inertia and the prediction of band contours for this molecule is not feasible. A study of the model, however, indicates that the symmetry axis will be the axis of intermmediate moment of inertia. Accordingly, bands of species a should have type B contours, while bands of species b should have contours that are hybrids between types A and C. There is considerable evidence from the infrared spectrum that gauche bands of species b have a PR separation of approximately 21 cm^{-1}.

It has been possible to make practically complete assignments of the vibrational fundamentals for both trans and gauche isomers. For brevity, the isomer, or isomers, to which a frequency is ascribed will not be stated explicitly in what follows but will be implied by the species assignment, a_g, a_u, b_g and b_u referring to the trans and a and b to the gauche isomers.

In the region near 3000 cm^{-1}, 4 fundamentals of each isomer associated with C-H stretching are expected. In the infrared spectrum of the gas 4 strong bands are found at 2895, 2951, 2966 and 2987 cm^{-1} and two weak shoulders at 2994 and 3001 cm^{-1}. Three Raman-active bands are found in this region: a strong polarized band at 2895 cm^{-1}, an extremely strong polarized band at 2962 cm^{-1} and a very broad, diffuse, slightly polarized band extending from about

2980 to 3005 cm^{-1}. The latter probably represents a superposition of two or more bands. The infrared bands at 3001, 2994 and 2987 cm^{-1} are interpreted as overlapping a_u, a and b fundamentals associated with asymmetrical C-H stretching, and the broad Raman band at 2980-3005 cm^{-1} in the liquid is assumed to represent the corresponding b_g fundamental overlapping with the a and b fundamentals. The very strong infrared band at 2966 cm^{-1} is interpreted as a b fundamental and the strong polarized Raman band at 2962 cm^{-1} are interpreted as overlapping a_g and b fundamentals. The very strong infrared band at 2951 cm^{-1} with no counterpart in the Raman spectrum is assigned as a b_u fundamental, while the strong infrared band at 2895 cm^{-1} and the polarized Raman band at the same wave number are interpreted as an a fundamental.

In the region from 1500 to 800 cm^{-1} nine fundamentals of each rotational isomer are expected, associated with C-F stretching, C-C stretching and CH_2F deformation. The fact that fewer than the expected number of bands are found, indicates that several of the observed frequencies are common to the trans and gauche isomers. The strong infrared band at 1462 cm^{-1} in the gas with a PR separation of 22 cm^{-1} and the very strong depolarized Raman band at 1456 cm^{-1} are assigned as a b fundamental. The weak polarized Raman band at 1416 cm^{-1} is interpreted as an a_g fundamental. The two strong infrared bands at 1415 and 1402 cm^{-1} are somewhat arbitrarily assigned as a_u and a fundamentals, respectively.

The strong infrared band with zero branch at 1376 cm^{-1} but rather complex contour caused in part by overlapping of other bands has no corresponding Raman band. It is assigned as a b_u fundamental. The medium intensity infrared band at 1295 cm^{-1} is assigned as a b fundamental and the depolarized Raman band at 1285 cm^{-1} as overlapping b_g and b fundamentals. The weak, approximately type B, infrared band with maxima at 1277 and 1271 cm^{-1} and the Raman band at 1272 cm^{-1} for which no polarization data are available, are interpreted as an a fundamental. The strong infrared band at 1246 cm^{-1} with PR separation 21 cm^{-1} and the depolarized Raman band at 1244 cm^{-1} are assigned as a b fundamental.

In the region around 1100 cm^{-1} there is considerable overlapping of infrared bands, which makes the interpretation difficult. On the other hand, when the solvent effect on the infrared bands and the temperature effect on the Raman bands of the liquid, to be described later, are utilized plausible assignments can be made.

The medium intensity infrared band at 1112 cm^{-1}, whose contour resembles that of a type B band, and the polarized Raman band at 1115 cm^{-1}, which is enhanced at lower temperatures, are interpreted as an a fundamental. The solvent effect indicates that the very strong infrared band at 1088 cm^{-1} belongs to the gauche isomer. It is assigned as an a fundamental. The strong polarized Raman band at 1079 cm^{-1} is interpreted as a superposition of this

a fundamental and an a_g fundamental. The very strong infrared band at 1065 cm^{-1} in the gas and at 1057 cm^{-1} in solution, is assumed from the solvent effect to belong to the trans isomer and is assigned as a b_u fundamental. The strong polarized Raman band at 1049 cm^{-1} is interpreted as an a_g fundamental.

The very strong infrared band at 897 cm^{-1} with PR separation 21 cm^{-1} is assigned as overlapping b_u and b fundamentals, and the strong depolarized Raman band at 881 cm^{-1} is interpreted as the b fundamental. This is supported by the conclusions drawn from the temperature and solvent effects that the Raman band belongs to the gauche isomer and the infrared band to both isomers.

The solvent effect indicates that the strong infrared band at 857 cm^{-1} belongs to the gauche isomer. In the Raman spectrum a highly polarized band occurs at 858 cm^{-1}, which is the strongest band in the spectrum next to that at 2962 cm^{-1}. The temperature effect indicates that it is caused primarily by the trans isomer. It is therefore interpreted as overlapping a_g and a fundamentals, the latter being responsible for the infrared absorption.

In the region below ca 850 cm^{-1}, 5 fundamentals are expected for each rotational isomer; the lowest of these should largely involve torsion and the others rocking motions. However, the torsional vibration of the trans isomer, of species a_u, will be unobservable, since it is

Raman-inactive and undoubtedly lies below the range of the CsBr prism.

The weak polarized Raman band at 804 cm^{-1}, which has no counterpart in the infrared spectrum, is assigned as an a_g fundamental. The very weak infrared band at 780 cm^{-1} and the faint Raman band at 768 cm^{-1} are, with some uncertainty, interpreted as an a fundamental. The weak Raman band at 669 cm^{-1} is assigned as a b fundamental. Since the sample contained a small amount of carbon dioxide, it was not possible to detect the infrared absorption that should occur at 669 cm^{-1}. The weak infrared band at 652 cm^{-1}, which has no counterpart in the Raman spectrum, is interpreted as a b_u fundamental. The strong infrared band at 498 cm^{-1} with PR separation 20 cm^{-1} and the depolarized Raman band at 502 cm^{-1} undoubtedly represent a b fundamental. The very weak Raman band at 450 cm^{-1} is interpreted as a b_g fundamental. The weak polarized Raman band at 329 cm^{-1} is assigned as an a fundamental. In the infrared, absorption occurs over a region from about 295 to 340 cm^{-1}. This is interpreted as an a_u fundamental overlapping the a fundamental just mentioned. Finally, the Raman band at 196 cm^{-1} is assigned as the a fundamental associated with torsion.

The assigned fundamentals are listed in Tables III and IV. The validity of these assignments may be tested by the sum rule derived by Mizushima, et al.[40] For the gauche isomer one finds $\sum_i \nu_i^2 = 49.36 \times 10^6$ and for the trans

isomer $\sum_i \nu_i^2 = 49.23 \times 10^6$, if one assumes that the unassigned lowest fundamental has the same value as for the gauche isomer. The fact that the sum is 0.3% lower for the trans than for the gauche isomer may result from the fact that half of the fundamentals for the trans isomer are obtained from the Raman spectrum of the liquid phase. The empirical sum rule of Bernstein and Pullin[41] is also quite well satisfied, the sums being $\sum_i \nu_i = 24{,}920$ for the gauche and $\sum_i \nu_i = 24{,}739$ for the trans isomer.

In terms of the assigned fundamentals it has been possible to interpret all of the observed Raman bands and practically all of the infrared bands. These interpretations are given in Tables V and VI. However, because of the large dependence of many of the frequencies upon the state of aggregation the correlation of several bands in the three spectra is difficult, and their interpretations are therefore rather uncertain. Most, if not all, of the very weak bands that have been left uninterpreted can be explained as ternary combination bands. However, in view of the large number of fundamentals, such interpretations are in most cases not unique and have therefore not been included in Table V.

Enthalpy Difference Between Rotational Isomers

All the stronger infrared bands assigned as fundamentals were recorded at 25°, 70°, 110°, 140° and 170°C with the aid of a 10-cm gas cell. While the bands became broader at higher temperatures, no change in the integrated extinction

of any band could be detected. The enthalpies of the two rotational isomers in the gaseous state must therefore be equal within the experimental error. A rough estimate based on Bernstein's graphical method[42] indicates that the upper limit of this error is approximately ± 200 cal/mole.

In the liquid state, on the other hand, the intensities of some of the Raman bands were found to vary with temperature. The Raman tube was surrounded by a vacuum jacket and was cooled by a stream of cold nitrogen. Sets of exposures of durations 20 min, 1 hr and 3 hrs were made at 35° and -25°C. Unfortunately, it was not possible to use lower temperatures, since the sample contained a small amount of an impurity which would freeze and make the sample turbid, thus producing a heavy background in the Raman spectrum.

The microphotometer traces of the Raman spectra showed that the bands at 881, 1115 and 1456 cm^{-1} were enhanced as the temperature was lowered, while the bands at 858 and 1049 cm^{-1} decreased in intensity with decreasing temperature. The photographic intensity data were not accurate enough to calculate ΔH^{o} for the liquid state. However, it was concluded that the bands at 881, 1115 and 1456 cm^{-1} are caused (at least predominantly) by the less stable isomer and the two other bands by the more stable isomer.

According to Onsager's theory of dielectrics,[43] the

polar gauche isomer should have lower potential energy in the liquid than in the gas, while the non-polar trans isomer should not suffer a change in potential energy on going from gas to liquid. Since the two isomers are found to have approximately the same energy in the gaseous state, the gauche form should be the more stable isomer in the liquid state. This is in accord with the assignments of the 5 Raman bands mentioned above: the 1456, 1115 and 881 cm^{-1} bands all have counterparts in the infrared spectrum and are ascribed to gauche, gauche, and gauche + trans (with gauche dominating), respectively; the 1049 cm^{-1} band, on the other hand, is assigned to the trans isomer, and the 858 cm^{-1} band, which has a counterpart in the infrared spectrum, is ascribed to both isomers (with the trans isomer dominating).

According to Onsager[43] a spherical molecule of radius R and dipole moment μ loses the potential energy

$$E_r = \frac{\varepsilon - 1}{2\varepsilon + 1} \frac{\mu^2}{R^3}$$

when transferred from vacuum ($\varepsilon = 1$) to a medium of dielectric constant ε. Using the bond moments $\mu_{C-H} = 0.4$, $\mu_{C-F} = 1.45D$[18], one finds the value 1.73 D for the dipole moment of the gauche isomer (the same as for $CHF_2 - CHF_2$), provided one assumes an ideal gauche form obtained from the trans form by rotating one of the CH_2F groups 120° with respect to the other. In the actual gauche molecule, the dipole moment is probably somewhat smaller. The trans molecule has a center of symmetry and has zero dipole moment. When the compound is dissolved in

solvents of different dielectric constants, the isomer equilibrium should change. This was verified by disolving $CH_2F - CH_2F$ in the following solvents: cyclohexane, carbon tetrachloride, chloroform, acetonitrile and nitromethane, the two first-mentioned being non-polar, the last two strongly polar, and chloroform having an intermediate polarity. It was necessary to use a thin cell, of thickness 0.0267 mm, in order to reduce the absorption of the polar solvents, and only such bands of the sample could be studied that are very strong and not overlapped by solvent bands. The intensities of the infrared bands at 861, 887, 1057 and 1087 cm^{-1} were measured at different concentrations in different solvents, and their relative intensities were compared. Since the sample is extremely volatile at room temperature, it was not possible to measure the concentrations used. The ratio between the extinctions of two bands was found to vary with the dielectric constant of the solvent in good agreement with Onsager's theory. From these variations it was concluded that the 861 and 1087 cm^{-1} bands are caused by the gauche and the 1057 cm^{-1} band by the trans isomer, while the band at 887 cm^{-1} is due to both isomers.

Since only relative displacements of the equilibrium between the rotational isomers in the different solvents can be obtained from the infrared data, the value for the ratio between the equilibrium concentration in one of the solvents, cyclohexane, was estimated as follows: It was assumed that

the ratio of gauche to trans isomer is 2:1 in the gaseous state. For cyclohexane, of dielectric constant 2.05, Onsager's formula then gives 2.54 for the ratio of the concentrations of the gauche and trans isomers. This value is then used in conjunction with the infrared data to determine the equilibrium ratios in the other solvents. When these ratios are plotted against the dielectric constant of the solvent, the upper curve shown in Fig. 19 is obtained. The lower curve is a theoretical curve, based on Onsager's formula and the values μ = 1.7 D and R = 1.6 A for the dipole moment and radius of the gauche isomer, respectively, and a simple Boltzmann factor. The experimental and theoretical displacements of the equilibrium are of the same order of magnitude, although the former are considerably larger than the latter. This is in accord with what was found for the conformational equilibrium of trans - 1,2-dihalogenocyclohexanes.[55] The dielectric constant of $CH_2F - CH_2F$ is not known, but it is probably not much different from the value 10 found for $CH_2Cl - CH_2Cl$.[44] If this is correct, the isomeric equilibrium in liquid $CH_2F - CH_2F$ should be intermediate between the equilibria in chloroform and nitromethane, and the enthalpy difference ΔH^o should be about 800 cal/mole.

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[55]P. Klaboe, J. J. Lothe and K. Lunde, Acta Chem. Scand. 11, 1677 (1957).

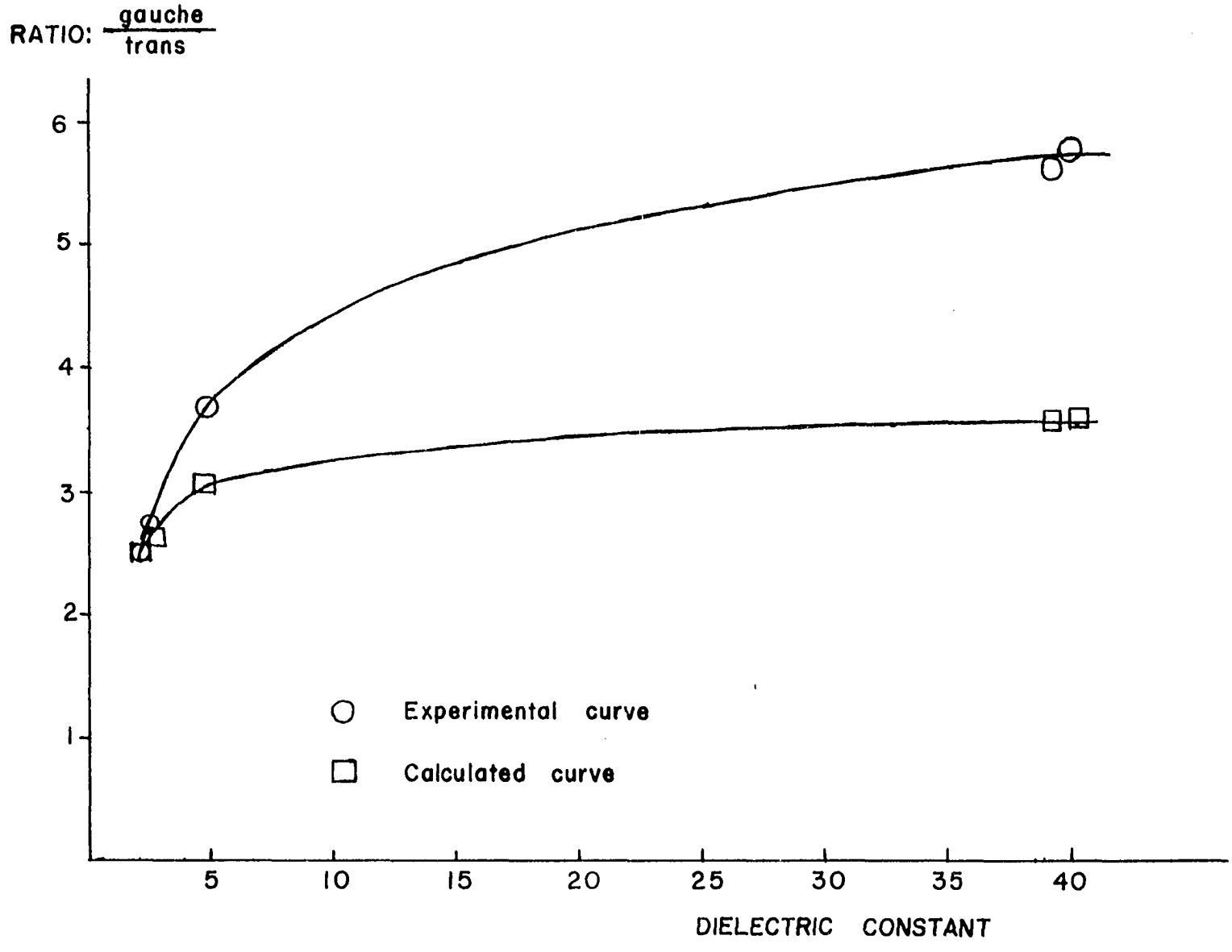

Fig. 19. Relative Values of C_{trans}/C_{gauche} as a Function of the Dielectric Constant of the Solvents

Comparison With $CH_2Cl - CH_2Cl$ and $CH_2Br - CH_2Br$

It is of great interest to compare the results obtained here with those previously reported for $CH_2Cl - CH_2Cl$ and $CH_2Br - CH_2Br$.[56] In both of these compounds the trans isomer has the lower enthalpy in the gaseous phase. Because of the stabilization of the gauche form in the liquid state, H^o (gauche) - H^o (trans) is smaller in this state. In the case of $CH_2Cl - CH_2Cl$ this difference is zero, and for $CH_2Br - CH_2Br$ it is ca 0.7 kcal/mole. As shown by the following table, the data obtained here for $CH_2F - CH_2F$ fit quite well with those for the two other compounds. It is

Compound	Phase	H^o (gauche) - H^o (trans)
$CH_2F - CH_2F$	gas	0 kcal/mole
	liquid	-0.8
$CH_2Cl - CH_2Cl$*	gas	1.15
	liquid	0
$CH_2Br - CH_2Br$*	gas	1.54
	liquid	0.72

*The values given for these compounds are averages of what are believed to be the most reliable of the previously reported values.[56]

seen that the gauche form becomes more stable as the substituted halogen changes from bromine to chlorine and from chlorine to fluorine. This is what would be expected if steric factors are largely responsible for the stability of the isomers, as assumed by Mizushima.[47] The different

[56]Reference 20, p. 41.

relative stabilities of the trans and gauche isomers for the three compounds may also in part explain their different behavior on crystallizing. The chloro- and bromo-compounds both crystallize in the trans form. In liquid $CH_2F - CH_2F$ the gauche isomer predominates, and the conversion to the trans form would require the addition of energy. Apparently, a mixed crystal of the two isomers is formed.

TABLE V

INFRARED SPECTRAL DATA FOR $CH_2F - CH_2F$ (in cm^{-1})

Gas		Liquid		Solid		
Wave Number	Description[a]	Wave Number	Description[a]	Wave Number	Description[a]	Interpretation
295-340	w					a_u + a fundamentals
487 498 507	s			506	s	b fundamental
652	w					b_u fundamental
780	vw					a fundamental
857	s	[861][b]	vs	862	vs	a fundamental
871	w					196 + 669 = 865 B
886 897 907	vs	[887]	vs	887	vs	b_u + b fundamentals
971	vw	954	vw			196 + 780 = 976 A
				1009	w	2 x 506 = 1012 A
1051	vw	1039	w			196 + 857 = 1053 A
1065	vs	[1057]	vs	1033	vs	b_u fundamental
1073	vw					
1088	vs	[1087]	vs	1061	vs	a fundamental
1112	m	1118	vw	1122	s	a fundamental
1234 1246 1255	s	1241	s	1240	s	b fundamental
1271 1277	w					a fundamental

TABLE V--Continued

Gas		Liquid		Solid		
Wave Number	Description[a]	Wave Number	Description[a]	Wave Number	Description[a]	Interpretation
1295	m	1283	m	1277	s	b fundamental
1326	vw					2 x 669 = 1338 A
1365 1376 1386	s	[1373]	m	1369	w	b_u fundamental
				1379	w	506 + 877 = 1383 A; ca 320 + 1061 = 1381 A
1402	s	[1406]	s	1406	w	a fundamental
1415	s			1423	s	a_u fundamental
1473 1462 1451	s	[1458]	s	1460	s	b fundamental
				1720	m	ca 320 + 1406 = 1726 A; 652 + 1061 = 1713 B_u
1761	w	1740	w	1738	m	498 + 1274 = 1772 B; 498 + 1246 = 1744 A
1927	vw					652 + 1285 = 1937 A_u
1963	w					857 + 1112 = 1969 A; 669 + 1295 = 1964 A
1982	m	1938	m,b			897 + 1088 = 1985 B
1996	w					897 + 1112 = 2009 B
2101	w					857 + 1246 = 2103 B
2152	m					857 + 1295 = 2152 B
2163	m					897 + 1274 = 2171 B; 2 x 1088 = 2176 A
2476	w					1065 + 1416 = 2481 B_u

TABLE V--Continued

Gas		Liquid		Solid		
Wave Number	Description[a]	Wave Number	Description[a]	Wave Number	Description[a]	Interpretation
		2532	vw			1241 + 1283 = 2524 A
2556	w	2561	vw			1274 + 1295 = 2569 B
2737	vw	2737	vw			
2746	m					1274 + 1462 = 2736 B
2759	m	2760	vw			1295 + 1462 = 2757 A
2796	w	2805	vw			1376 + 1416 = 2792 B_u
2813	m	2829	vw			1415 + 1416 = 2831 A
2895	s	[2887]	s	2901	s	a fundamental
2951	vs			2980	vs	b_u fundamental
2966	vs	[2953]	vs	3010	w	b fundamental
2987	vs	[2982]	vs	3018	vs	b fundamental
2994	w					a_u + a fundamentals
3001	w					
		3015	w			
3067	w					196 + 2895 = 3091 A
3106	w					
3318	w					ca 320 + 2994 = 3314 A; ca 320 + 2987 = 3307 B
3476	w	3494	vw			498 + 2987 = 3485 A
3843	vw	3837	vw			857 + 2987 = 3844 B; 897 + 2962 = 3859 B_u
3982	vw	4010	vw			1088 + 2895 = 3983 A

TABLE V--Continued

Gas		Liquid		Solid		
Wave Number	Description[a]	Wave Number	Description[a]	Wave Number	Description[a]	Interpretation
4067	m	4072	w			1079 + 2994 = 4073 A_u; 1088 + 2987 = 4075 B; 1112 + 2966 = 4078 B
4218	vw					1246 + 2987 = 4233 A
		4237	vw			1241 + 2994 = 4235 B
4270	vw					1295 + 2987 = 4282 A; 1285 + 2994 = 4279 B_u
4338	vw					1376 + 2962 = 4338 B_u; 1462 + 2895 = 4357 B
4417	m	4425	m			1462 + 2966 = 4428 A; 1462 + 2987 = 4449 A
5692	vw					
5784	vw					2 x 2895 = 5790 A

[a]For the meaning of the abbreviations used, see footnotes to Table I.

[b]Wave numbers enclosed in brackets are obtained in carbon tetrachloride solution.

TABLE VI

RAMAN SPECTRAL DATA FOR LIQUID $CH_2F - CH_2F$

Wave Number	Description[a]	Depolarization	Exciting Hg lines[b]	Interpretation
196	vw		e	a fundamental
329	w	0.3	e	a fundamental
450	vw		e	b_g fundamental
502	w	0.8	e	b fundamental
669	vw		e	b fundamental
768	vw		e	a fundamental
804	w	p	e	a_g fundamental
858	vvs,sh	0.09	e,k,i	a_g + a fundamentals
881	vs	0.8	e,k,i	b fundamental
1049	s	0.5	e	a_g fundamental
1079	s,d	0.5	e,k	a_g + a fundamentals
1115	m	0.09	e	a fundamental
1244	s	0.8	e,k	b fundamental
1272	m,d		e	a fundamental
1285	s	0.8	e,k	b_g + b fundamentals
1416	w	0.5	e	a_g fundamental
1456	vs	0.7	e,k	b fundamental
2733	m	p	e	2 x 1373 = 2746 A_g
2806	m	p	e	2 x 1406 = 2812 A
2826	w	p	e	2 x 1416 = 2832 A_g
2895	s,sh	0.2	e,k,i	a fundamental
2962	vvs,sh	0.1	e,k,i	a_g + b fundamentals

TABLE VI--Continued

Wave Number	Description[a]	Depolarization	Exciting Hg lines[b]	Interpretation
ca 2990	s,vd	0.7	e	b_g + a + b fund

[a]For the meaning of the abbreviations used see footnotes to Table II.

[b]For the meaning of the Kohlrausch symbols see footnotes to Table II.

TABLE VII

FUNDAMENTAL VIBRATIONAL FREQUENCIES
FOR trans $CH_2F - CH_2F$ (in cm^{-1})[a]

Species	Infrared			Raman	Approximate Motion
	Gas	Liquid	Solid	Liquid	
a_g				2962 vvs (0.1)	C-H stretch
a_g				1416 w (0.5)	CH_2F deform
a_g				1079 s (0.5)	CH_2F deform
a_g				1049 s (0.5)	C-F stretch
a_g				858 vvs (0.09)	C-C stretch
a_g				804 w (p)	Rocking
a_u	ca2994 w				C-H stretch
a_u	1415 s		1423 s		CH_2F deform
a_u	ca 320 w				Rocking
a_u	-				Torsion
b_g				ca2990 s (0.7)	C-H stretch
b_g				1285 s (0.8)	CH_2F deform
b_g				450 vw	Rocking
b_u	2951 vs		2980 vs		C-H stretch
b_u	1376 s	[1373] [b] m	1379 w		CH_2F deform
b_u	1065 vs	[1057] vs	1033 vs		C-F stretch
b_u	897 vs	[887] vs	877 vs		CH_2F deform
b_u	652 w				Rocking

[a]For the meaning of the abbreviations used, see footnotes to Table I.

[b]Wave numbers enclosed in brackets are obtained in carbon tetrachloride solution.

TABLE VIII

FUNDAMENTAL VIBRATIONAL FREQUENCIES
FOR gauche $CH_2F - CH_2F$ (in cm^{-1})[a]

Species	Infrared			Raman	Approximate Motion
	Gas	Liquid	Solid	Liquid	
a	ca2994 w			ca2990 s (0.7)	C-H stretch
a	2895 s	[2887] [b] s	2901 s	2895 s (0.2)	C-H stretch
a	1402 s	[1406] s	1406 w		CH_2F deform
a	1274 w			1272 m	CH_2F deform
a	1112 m	1118 vw	1122 s	1115 m (0.09)	CH_2F deform
a	1088 vs	[1087] vs	1061 vs	1079 s (0.5)	C-F stretch
a	857 s	[861] vs	862 vs	858 vvs (0.09)	C-C stretch
a	780 vw			768 vvw	Rocking
a	ca 320 w			329 w (0.3)	Rocking
a				196 vw	Torsion
b	2987 vs	[2982] vs	3018 vs	ca2990 s (0.7)	C-H stretch
b	2966 vs	[2953] vs	3010 vs	2962 vvs (0.1)	C-H stretch
b	1462 s	[1458] s	1460 s	1456 vs (0.7)	CH_2F deform
b	1295 m	1283 m	1277 s	1285 s (0.8)	CH_2F deform
b	1246 s	1241 s	1240 s	1244 s (0.8)	C-F stretch
b	897 vs	[887] vs	877 vs	881 s (0.8)	CH_2F deform
b				669 vw	Rocking
b	498 s		506 s	502 w (0.8)	Rocking

[a]For the meaning of the abbreviations used, see footnotes to Table I.

[b]Wave numbers enclosed in brackets are obtained in carbon tetrachloride solution.

CHAPTER V

INFRARED AND RAMAN SPECTRA OF $CF_2Cl - CHF_2$ AND $CF_2Br - CHF_2$

Introduction

It was mentioned in chapter I that a number of halogenated ethanes with asymmetrical end-groups have been studied in the past, particularly by Mizushima,[20] Bernstein[26,28,38] and Kagarise.[27,29] The Raman[57] and infrared[58] spectra of $CF_2Cl - CHF_2$ in the liquid state have been obtained, but no data have been reported for $CF_2Br - CHF_2$. In the present chapter infrared and Raman spectral data are reported for $CF_2Cl - CHF_2$ and $CF_2Br - CHF_2$. The vibrational spectra of the two compounds show striking similarities. Both compounds exhibit rotational isomerism in the gaseous, liquid and solid states. In both compounds, the enthalpy-difference between the two rotational isomers (ΔH^o) is approximately equal to zero. Partly because of this fact, no really reliable way

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[57] G. Glockler and C. Sage, J. Chem. Phys. 9, 387 (1941).

[58] NRL Report 3924. Infrared Spectra of Fluorinated Hydrocarbons (Naval Research Laboratory, Washington, D.C., 1952).

was found to distinguish between the vibrational fundamentals of the two isomers either in $CF_2Cl - CHF_2$ or in $CF_2Br - CHF_2$. A complete assignment of the vibrational fundamentals of the two compounds could therefore not be made.

Experimental Results

The samples of $CF_2Cl - CHF_2$ (bp - 15°C at 746 mm) and $CF_2Br - CHF_2$ (bp 12-13°C at 746 mm), hereafter called (C) and (B), respectively, were both prepared and purified in the laboratory of Professor A. L. Henne at Ohio State University. The spectra indicate that the purity of both samples is high, except that the sample of (C) contains a considerable amount of carbon dioxide.

The infrared absorption spectra of the gases at room temperature were obtained according to the procedure described in chapter II. In order to study eventual intensity variations with temperature, the infrared spectra of the gases were recorded at 30°, 70°, 110°, 150° and 180°C with an electrically heated cell[13] of length 10 cm. The infrared spectra of the two compounds in the solid state at -180°C were obtained with a low temperature cell[13] which was a modification of one described by Lord.[33] The infrared spectrum of (C) in the gaseous state is shown in Figs. 20-22, the spectrum of (B) in Figs. 23-25. The wave numbers of the observed absorption maxima (or in some cases "shoulders") are listed in Tables X and XI, respectively.

The Raman spectra of the liquids, contained in

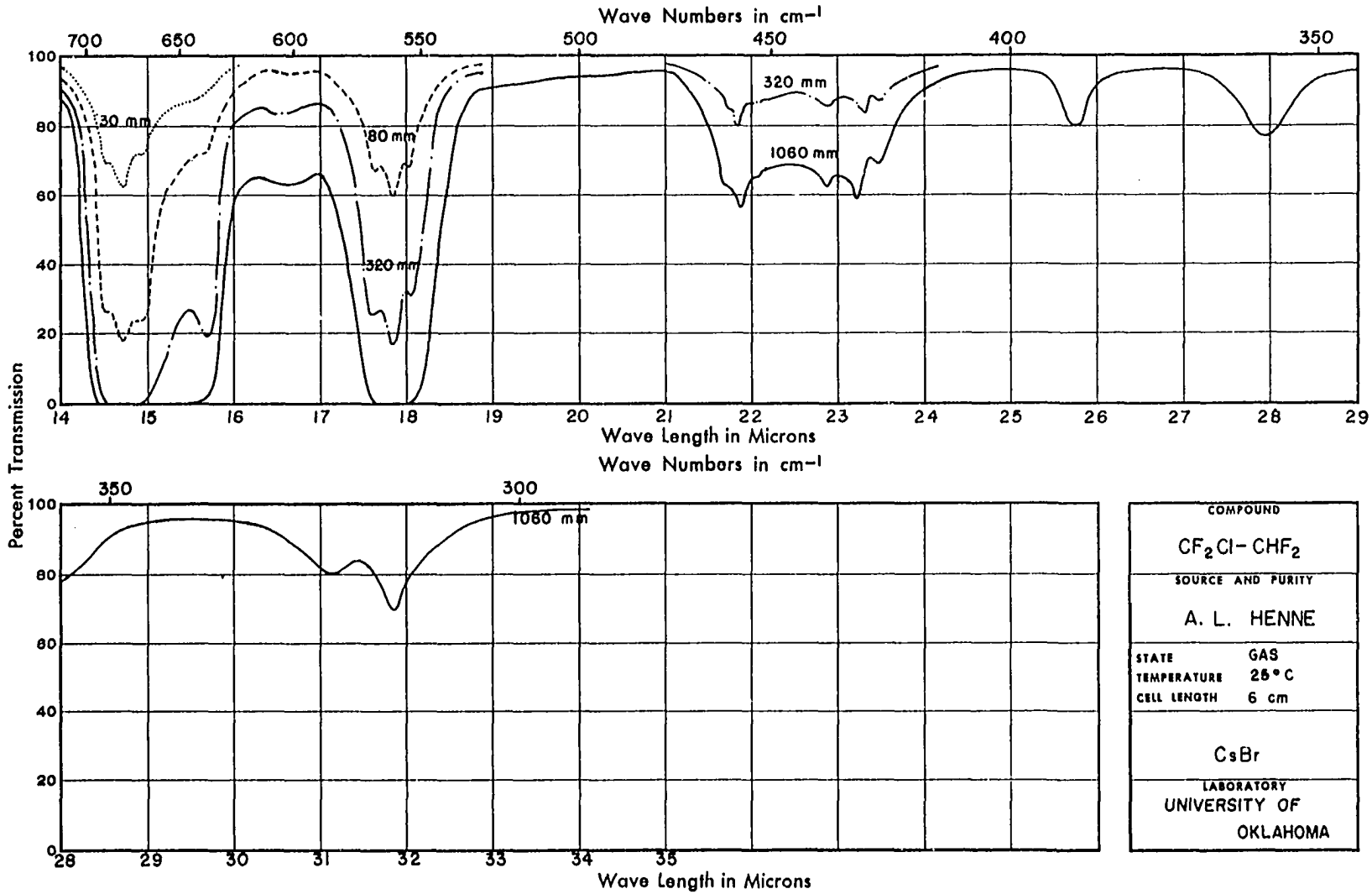

Fig. 20. Infrared Spectrum of Gaseous CF_2Cl-CHF_2 (CsBr Region)

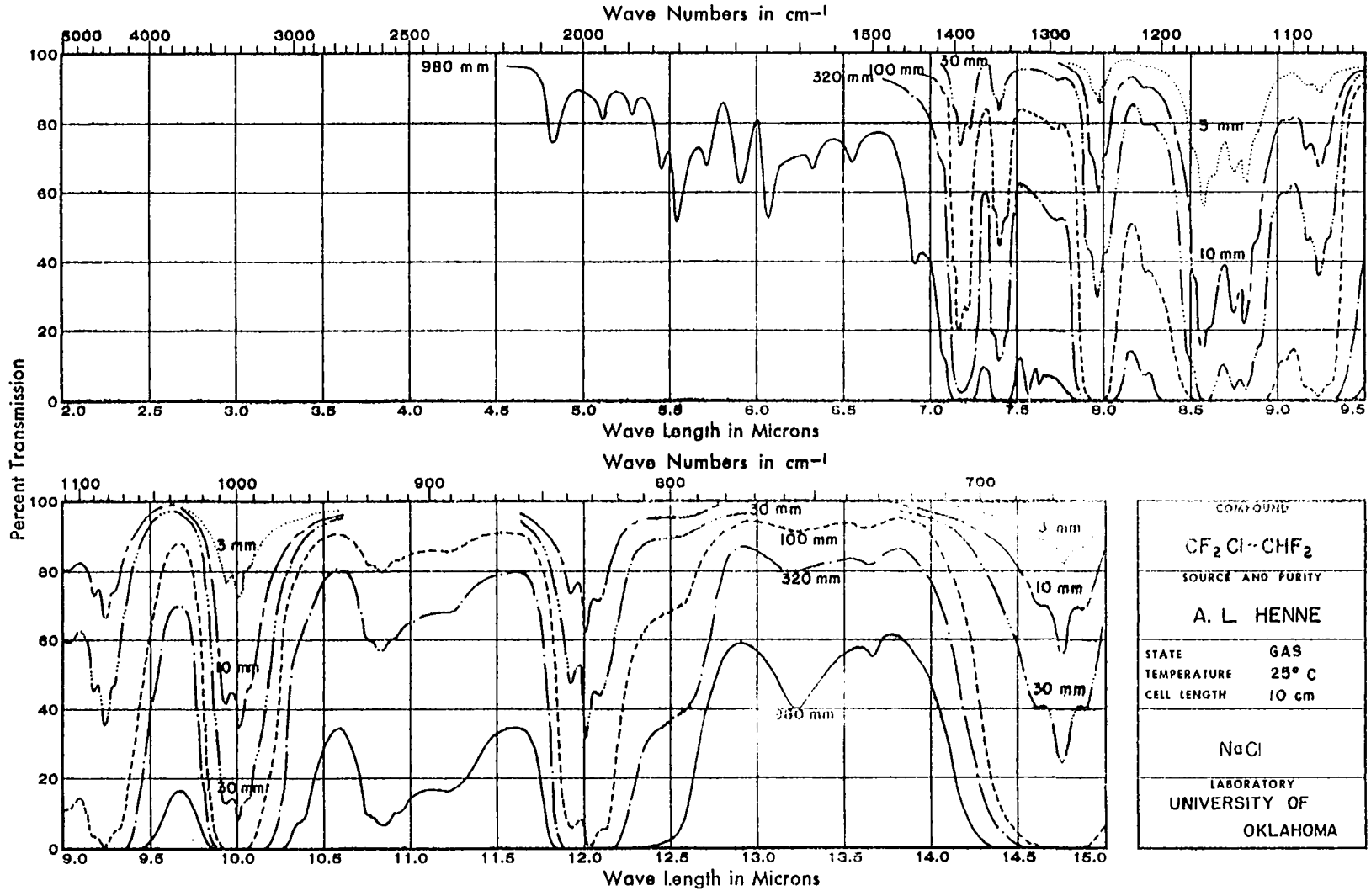

Fig. 21. Infrared Spectrum of Gaseous CF_2Cl-CHF_2 (NaCl Region)

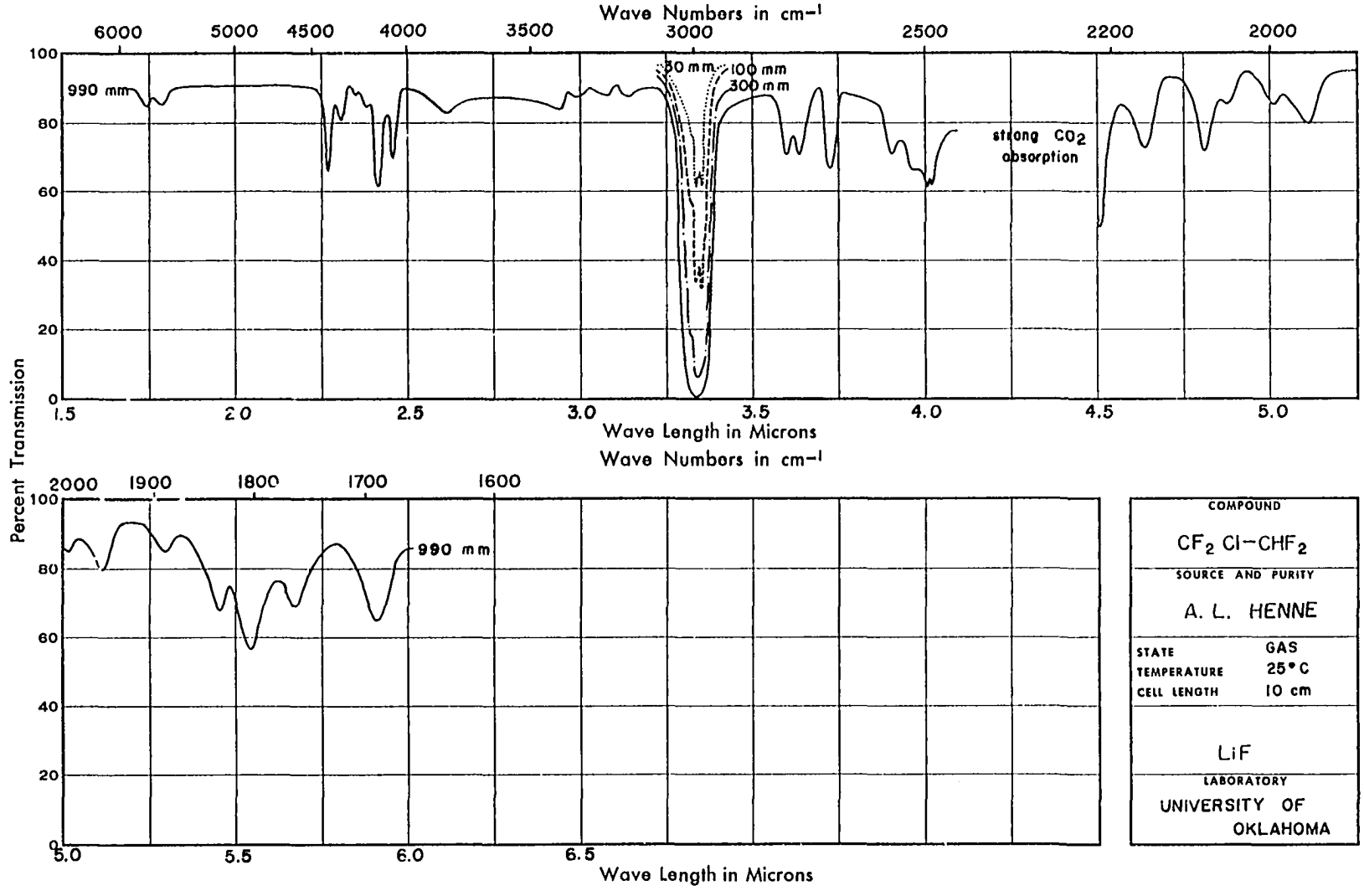

Fig. 22. Infrared Spectrum of Gaseous CF_2Cl-CHF_2 (LiF Region)

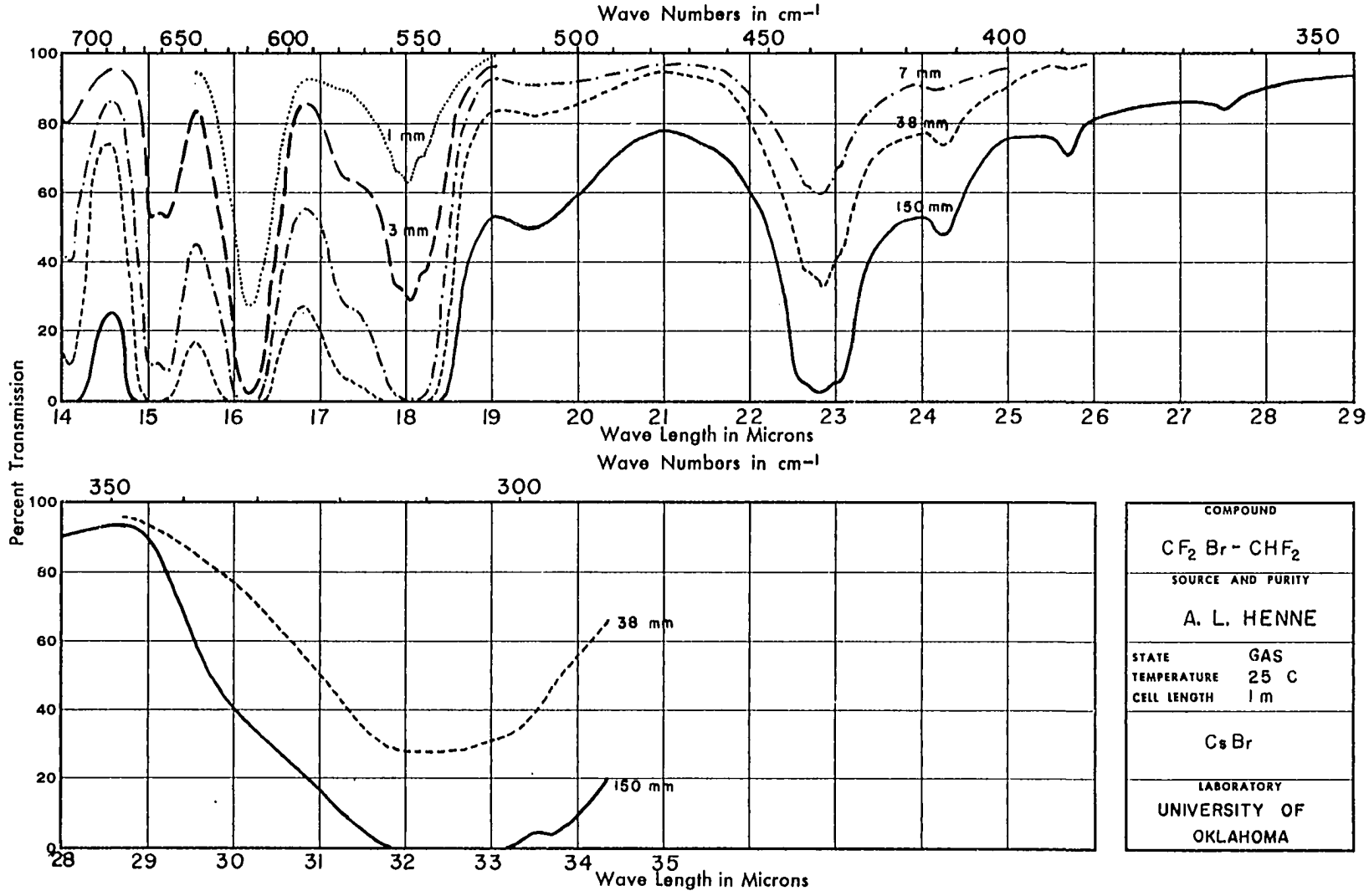

Fig. 23. Infrared Spectrum of Gaseous CF_2Br-CHF_2 (CsBr Region)

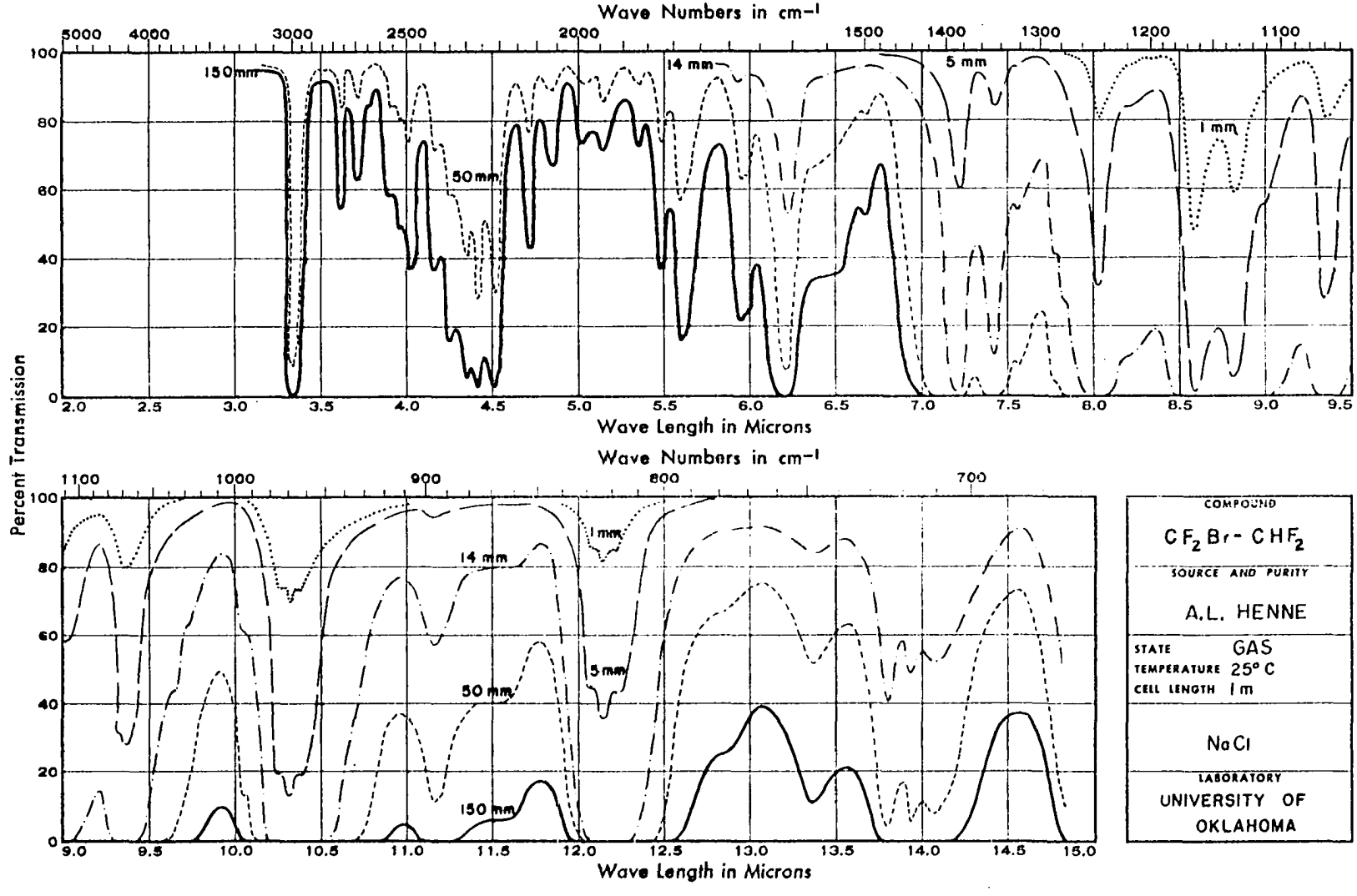

Fig. 24. Infrared Spectrum of Gaseous CF_2Br-CHF_2 (NaCl Region)

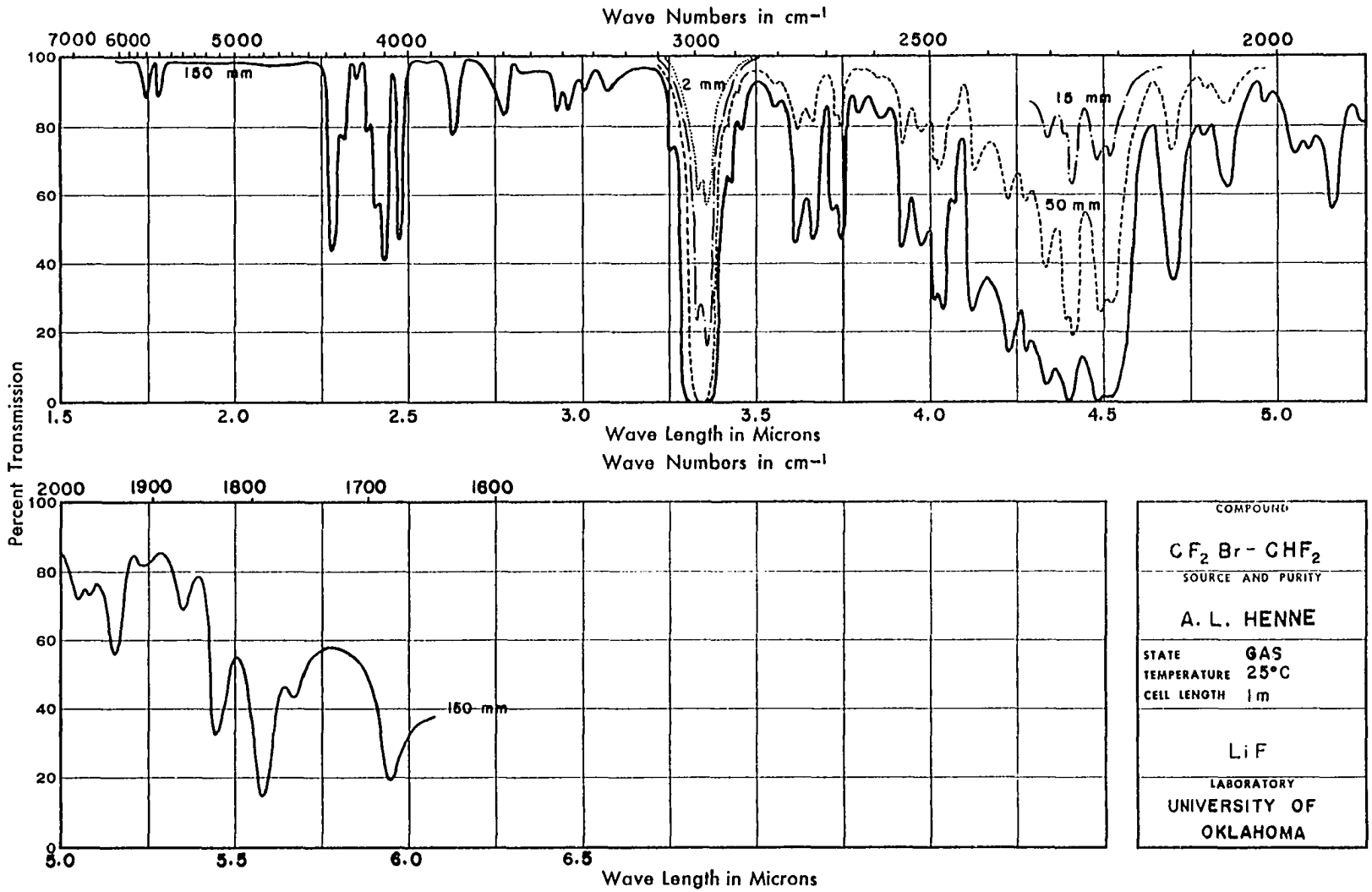

Fig. 25. Infrared Spectrum of Gaseous CF_2Br-CHF_2 (LiF Region)

sealed Pyrex tubes, were photographed as described in chapter II. Furthermore, Raman spectra of the liquids at low temperatures were obtained by a method described by Jackson.[37] Identical sets of exposures were made at 30°, -30° and -80°C and the intensities of the bands were compared from photometer curves. The polarization ratios were measured for the strong Raman bands by the Crawford and Horwitz[36] method. The Raman spectral data for (C) and (B) are listed in Tables XII and XIII, respectively. Certain discrepancies exist between the Raman bands observed by Glockler and Sage[57] for $CF_2Cl - CHF_2$ and those observed here. A very weak band at 910.2 cm^{-1} and an uncertain band at 93.0 cm^{-1} reported by Glockler and Sage were not observed in the present work. On the other hand, 8 bands, most of them weak and diffuse, were observed in the present study but were not reported by Glockler and Sage.

Interpretation

It was mentioned in chapter I that all the information available about halogenated ethanes indicates that these molecules exist in staggered configurations only. As explained in chapters III and IV the vibrational spectra of $CHF_2 - CHF_2$ and $CH_2F - CH_2F$ show these compounds to exist as equilibrium mixtures of rotational isomers of symmetries C_{2h} (trans) and C_2 (gauche). The large number of strong infrared and Raman bands observed for $CF_2Cl - CHF_2$ and $CF_2Br - CHF_2$ indicates that these compounds consist of rotational isomers.

The probable isomeric configurations of (C) and (B) are a "trans" form having the symmetry C_s, and two enantiomorphic "gauche" forms obtained from the "trans" form by rotating one of the end-groups approximately 120°. The "gauche" form has no symmetry element i.e. belongs to point-group C_1.

The 18 normal vibrations of the molecules of symmetry C_s divide into 11 a' and 7 a". The former should be polarized in the Raman spectrum, while the latter should be depolarized. All vibrations of the "gauche" molecules belong to the same species, so no information can be obtained from depolarization measurements. Assuming the interatomic distances C-C = 1.54, C-F = 1.37, C-H = 1.093, C-Cl = 1.77 and C-Br = 1.98A, and tetrahedral angles, one obtains for the "trans" form of (C) and (B) the principal moments of inertia listed in Table IX. Since the "trans" forms of (C) and (B) are both approximately symmetrical tops, Gerhard and Dennison's[54] as well as Badger and Zumwalt's[39] curves can be used to predict the band contours. The largest moment is about an axis perpendicular to the symmetry plane. Thus infrared bands of species a" should have type C contours, while infrared bands of species a' should have contours that are hybrids between A and B. The predicted PR separations are given in Table IX. Since the "gauche" form has no symmetry element other than the identity, no predictions can be made about the contours of the bands belonging to this form.

All the fundamental frequencies except the one

TABLE IX

PRINCIPAL MOMENTS OF INERTIA, BAND CONTOURS AND PR SEPARATIONS FOR INFRARED BANDS OF THE "trans" FORMS OF $CF_2Cl - CHF_2$ AND $CF_2Br - CHF_2$

		$CF_2Cl - CHF_2$		$CF_2Br - CHF_2$	
	I_x	335.0×10^{-40} gem^2		394.4×10^{-40} gem^2	
	I_y	455.4		606.1	
	I_z	474.4		684.8	
Angle of C-C bond with x-axis		$1^o59'$		$37^o36'$	
	Type	A	B	A	B
a'	PR sep[a]	10 cm^{-1}	11 cm^{-1}	10 cm^{-1}	12 cm^{-1}
	PR sep[b]	14 cm^{-1}		12 cm^{-1}	
	Type	C		C	
a"	PR sep[a]	14 cm^{-1}		14 cm^{-1}	
	PR sep[b]	16 cm^{-1}		13 cm^{-1}	

[a]Badger and Zumwalt, see reference 39.

[b]Gerhard and Dennison, see reference 54.

connected with C-H stretching are expected to lie below 1450 cm^{-1}. Since the number of strong and medium infrared bands, and also the number of Raman bands found in this region, greatly exceeds 17 for both (C) and (B), both compounds must exist as an equilibrium mixture of rotational isomers. The number of observed bands which appear to be fundamentals is about 26 for each compound. It is evident, therefore, that in many cases corresponding fundamentals belonging to

different isomers will not be sufficiently separated to appear as separate bands in the infrared and Raman spectra. This overlapping of a considerable number of corresponding fundamentals belonging to the "trans" and "gauche" isomers may be expected from the very close geometrical similarity between the two isomeric forms. Since a large number of the observed bands are superpositions of fundamentals belonging to different isomers, the Raman depolarization data and the infrared band contours are of little help in assigning fundamentals.

No way has been found to determine without considerable uncertainty whether an observed band belongs to the "trans" isomer, the "gauche" isomer or is a superposition of "trans" and "gauche" bands. The infrared spectra of the solids at -180°C do not appear significantly different from the spectra of the gases, and hence are of limited value for differentiating between the fundamentals of different isomers. Neither is the equilibrium between the rotational isomers in the gaseous or liquid states sufficiently displaced with change in temperature to provide a basis for such differentiation. The method of displacing the equilibrium by dissolving the samples in solvents of different polarities, which has been successful in certain cases,[20] could not be utilized except at low temperatures due to the volatility of both compounds. As will be discussed later, a large displacement of the isomeric equilibrium in solvents

of different polarity cannot be expected for the present molecules on the basis of Onsager's dielectric theory.[43]

In principle, it should be possible from observations of the combination bands that occur in the spectra to determine which fundamentals belong to the same isomeric form. However, the frequency differences between corresponding bands of the two rotational isomers are usually quite small. Observed combination bands can therefore in many cases be interpreted in different ways, thus making the evidence ambiguous.

While none of the strong infrared bands present in the gaseous state disappear in the spectra of the solid state, the relative intensities of a number of bands change considerably. It is not known if the intensity variations from gas to solid are due merely to changes in extinction coefficients caused by intermolecular interactions in the solid state, or if the intensity variations are caused by a shift in the isomeric equilibrium. It is important to note that in the region from approximately 800 to 1400 cm^{-1}, where the spectra of (C) and (B) are strikingly similar, corresponding bands in the spectra of the two components also behave in the same way upon solidification. Thus, if the intensity variation is caused by a displacement of the equilibrium, bands that increase in intensity should belong to one isomer, and bands that decrease should belong to the other isomer.

The two very strong infrared bands at 2987 and 3001 cm^{-1} in the spectrum of gaseous $CF_2Cl - CHF_2$ have somewhat uncertain PQR contours with PR separations of approximately 15 and 10 cm^{-1}, respectively. They must represent the single C-H stretching mode for each isomer. Corresponding bands are found at 2977 and 2998 cm^{-1} in the infrared spectrum of $CF_2Br - CHF_2$, the contours being even less well resolved. The corresponding Raman bands are very broad, with maxima at 2995 and 2990 cm^{-1} for (C) and (B), respectively. Instead of the terms "trans" and "gauche" the non-committal designations I and II will be used to describe the isomers. In the case of (C), I is defined as the isomer having a C-H stretching mode at 2987 cm^{-1}, while II is defined as the isomer having a C-H stretching mode at 3001 cm^{-1}. Correspondingly, I and II of (B) are defined as the isomers causing the bands at 2977 and 2998 cm^{-1}, respectively.

The 5 fundamentals for each isomer associated with C-F and C-C stretching and the highest of those associated with CHF_2 deformation are expected to lie in the region from 1400 to 800 cm^{-1}. There is a complete and very striking similarity between the infrared as well as the Raman spectra of (C) and (B) in this region. Corresponding bands in the spectra of (C) and (B) are of nearly the same intensity. Their positions are generally displaced somewhat towards longer wavelengths on going from (C) to (B). Ten strong or medium bands which all appear to be fundamentals are found

in this region for both (C) and (B). It appears, therefore, that four fundamentals are at somewhat different positions in the two isomers, while two fundamentals have the same, or very nearly the same, positions in each isomer.

The combination bands appearing above 4000 cm^{-1} may give a clue to the differentiation of the fundamentals of the two isomers in the region around 1200 cm^{-1}. The bands observed at 4198, 4252, 4338 and 4403 cm^{-1} in gaseous (C) are undoubtedly combinations between 1214, 1255, 1352 and 1396 cm^{-1}, on the one hand, and 2987 and 3001 cm^{-1} on the other. The bands at 1214 and 1352 cm^{-1} combine with 2987 cm^{-1} to give 4198 and 4338 cm^{-1}; 1255 and 1396 cm^{-1} combine with 3001 cm^{-1} to give 4252 and 4403 cm^{-1}. Therefore, 1214 and 1352 cm^{-1} are fundamentals belonging to the same isomer as 2987 cm^{-1}, i.e. the isomer denoted by I; 1255 and 1396 cm^{-1}, on the other hand, belong to isomer II. The fact that the corresponding frequencies in the spectrum of (B) can be classified in an entirely analogous manner, 1207 and 1348 cm^{-1} being I-bands, and 1245 and 1384 cm^{-1} II-bands, suggests that this explanation has a physical reality and is not due to coincidences. It is interesting to note that of these four infrared bands of (C), or of (B), those assigned to the I-isomer show a relative increase, while those assigned to the II-isomer show a decrease on going from gas to solid. It would seem, therefore, that the intensity variations are due to a displacement in the isomeric equilibrium on

solidification.

The assignments of the fundamentals between 800 and 1150 cm^{-1} have been made on the basis of band contours, polarization data and intensity-variations on transition to the solid state. Since the spectra of (C) and (B) are so similar, only the spectrum of (C) will be discussed. The very strong infrared band at 1169 cm^{-1} with PR separation 14 cm^{-1} is certainly a fundamental. It has lower relative intensity in the solid than in the gas, and has therefore been ascribed to II. The very strong infrared bands at 1138 and 1082 cm^{-1} have PR-separations 8 and 14 cm^{-1}, respectively, and have diffuse but polarized counterparts in the Raman spectrum. They both increase in relative intensity on going to the solid state and are therefore assigned as fundamentals of I. The very strong infrared band at 999 cm^{-1} having a PR separation of 14 cm^{-1} and decreasing in relative intensity on going to the solid state, corresponds to a weak depolarized Raman band at 995 cm^{-1}. These bands are assigned as a fundamental of II. The strong infrared bands at 922 and 833 cm^{-1} have PR separations 15 and 13 cm^{-1} and the latter corresponds to a very strong, polarized Raman band at 828 cm^{-1}. They do not change significantly in relative intensity by transition to the solid state and have both been assigned as overlapping fundamentals of I and II. The assignment of the corresponding fundamentals of (B) is made in exactly the same manner.

In the remaining, low frequency part of the spectrum 11 fundamentals of each isomer should occur. Of these, one should be associated largely with the C-Cl (Br) stretching, 2 with CHF_2 deformation, 3 with CF_2Cl (Br) deformation, 4 with rocking motions and one with torsion. As expected, the similarity between the spectra of (C) and (B) is less pronounced in this region. For either compound only 13 or 14 infrared or Raman bands strong enough to be considered as fundamentals are found. It seems evident, therefore, that most fundamentals of the two isomers overlap in this region. Although insufficient information is available to justify a complete assignment, a discussion of some of the bands in this region seems appropriate. The very strong band at 718 cm^{-1} in the infrared spectrum of (B) and the very weak Raman band at 711 cm^{-1} are assigned as overlapping fundamentals of I and II. The corresponding fundamentals of (C) are believed to occur at 800 cm^{-1}. The very strong infrared band at 678 cm^{-1} and the intense, broad Raman band at 672 cm^{-1} in the spectra of (C) are also interpreted as overlapping fundamentals of the two isomers. The width of this Raman band is probably a chlorine isotope effect. The frequency is somewhat low for C-Cl stretching, indicating that the vibration is of a mixed nature.

In the infrared spectrum of (B) two strong maxima are found near 660 cm^{-1} both in gas and solid. Although only a single sharp band is found in the Raman spectrum, it

is assumed that the splitting in the infrared results from the presence of two rotational isomers. The two very strong polarized Raman bands at 623 and 614 cm^{-1} in the spectrum of (B) corresponds to the single strong infrared band at 618 cm^{-1}. These bands are assumed to be fundamentals of I and II, respectively, associated mainly with CH_2F deformation. The infrared band of (C) at 561 cm^{-1} having a PR separation of 12 cm^{-1}, undoubtedly corresponds to the infrared band at 554 cm^{-1} with PR separation 10 cm^{-1} in (B). The corresponding Raman bands are sharp, polarized and of medium intensity. These bands have somewhat arbitrarily been taken as a fundamental of II involving CHF_2 deformation. The Raman bands at 514 and 504 cm^{-1} in the spectra of (C) and (B), respectively, of which an infrared counterpart is observed only in (B), are assumed to represent the corresponding fundamental of I. The medium infrared band at 457 cm^{-1} and the Raman band at 458 cm^{-1} of (C) and the corresponding bands in (B) near 438 cm^{-1} are assigned as overlapping I and II fundamentals associated with CF_2Cl (Br) deformation. The very strong Raman band of (C) at 432 cm^{-1}, with a strong counterpart in the infrared spectrum, is very broad and is therefore assumed to represent overlapping fundamentals of I and II. The corresponding fundamentals of (B) are believed to lie near 365 cm^{-1}. In the infrared spectrum of gaseous (C) there occurs a weak band at 358 cm^{-1} which appears to be split into two components in the infrared spectrum of the solid

and has a medium intensity counterpart in the Raman spectrum. It is interpreted as overlapping fundamentals of I and II. The corresponding fundamentals of (B) are assumed to lie at 332 cm^{-1}.

The medium intensity Raman band of (C) at 340 cm^{-1} and the strong infrared and Raman bands of (B) at 307 and 312 cm^{-1}, respectively, are assumed to be a fundamental of II. The infrared and Raman bands of (C) at 321 cm^{-1} and the Raman band of (B) at 299 cm^{-1} are assigned as the corresponding fundamental of I.

The bands below 300 cm^{-1} lie outside the range of the CsBr prism and are therefore observed only in the Raman spectra. Although some of these bands are very weak they are all assumed to be fundamentals. The bands at 253 and 231 cm^{-1} in (C) are somewhat arbitrarily assigned as fundamentals of II and I, respectively. In (B) the corresponding fundamentals appear to overlap at 182 cm^{-1}. The Raman bands at 196 cm^{-1} in (C) and at 165 cm^{-1} in (B) are assigned as overlapping fundamentals of I and II. These fundamentals and those below 400 cm^{-1} mentioned above, are undoubtedly associated with rocking motions.

The lowest Raman frequency, 138 cm^{-1}, observed for (C) probably represents overlapping fundamentals of I and II involving mainly torsion. The corresponding fundamentals of (B) have not been observed, undoubtedly because of the rather strong background near the exciting mercury line.

The assigned fundamentals are listed in Table XIV. In Fig. 26 is shown a correlation diagram of the assigned fundamentals in the series: CHF_2 - CHF_2 (chapter III, gauche form), CF_3 - CHF_2,[59] CF_2Cl - CHF_2 and CF_2Br - CHF_2. The vertical lines in Fig. 26 represent fundamentals; their position is determined from the infrared spectra of the gas, or if no infrared bands have been determined, from the Raman spectra of the liquid. The heights of the lines indicate the intensity of the infrared (or Raman) band. Fundamentals of (C) and (B) assigned to different isomers but representing similar vibrational modes are connected together. Corresponding fundamentals of the different molecules are joined by straight lines.

In terms of the assigned fundamentals it has been possible to assign all of the observed Raman bands and practically all of the infrared bands in the spectra of (C) and (B). The assigned infrared bands of (C) and (B) are listed in Tables X and XI, respectively, while the assigned Raman bands are listed in Tables XII and XIII. However, because of the large dependence of many of the frequencies upon the state of aggregation, the correlation of several bands in the different spectra is difficult. Most, if not all, of the weak bands that have been left uninterpreted can be explained as ternary combination bands.

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[59] J. Rud Nielsen, H. H. Claassen and N. B. Moran, J. Chem. Phys. 23, 329 (1955).

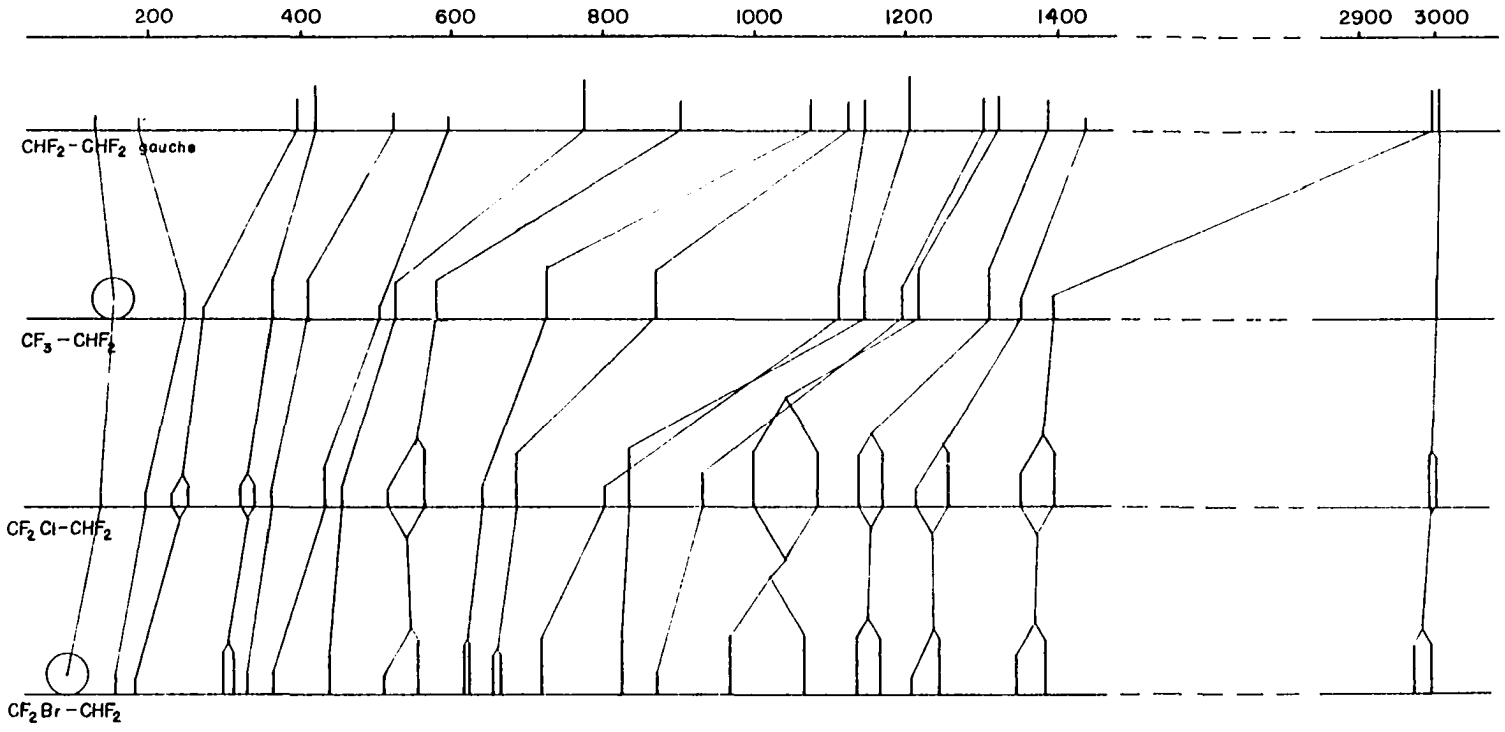

Fig. 26. Correlation Diagram of CF_2H-CF_2H, CF_3-CHF_2, CF_2Cl-CHF_2 and CF_2Br-CHF_2

However, in view of the large number of fundamentals, such interpretations are in most cases not unique and have therefore not been included in Tables X and XI.

There is no information available to decide which of the isomeric forms I and II is "trans" and which "gauche." No classification of the fundamentals assigned to I and II into species are made. An assignment of the species a' and a" has a meaning for the "trans" form only; in the "gauche" form all fundamentals belong to the same species (a).

Enthalpy Difference Between the Rotational Isomers

Attempts were made to determine the enthalpy difference ΔH^{o} between the rotational isomers by observing changes in the intensities of the infrared and Raman bands with temperature. However, no appreciable intensity variation of the infrared bands of either compound in the gaseous state was observed when the temperature was raised from 30° to 180°C. For the C-H stretching bands near 3000 cm^{-1} and some of the bands in the 1100 - 1400 cm^{-1} region very accurate extinction measurements were made at many positions in each band by means of a densitometer without observing any distinct temperature effect. Thus, the enthalpy difference between the rotational isomers of (C) and (B) in the gaseous state is very small. An estimate based on the graphical method of Bernstein[42] indicates that ΔH^{o} (gas) $<$ 200 cal/mole.

Identical sets of Raman exposures of the liquid were made at 30°, -30° and -80°C. The microphotometer curves

showed no observable temperature variation of any band of either compound. Thus, the enthalpy difference between the isomers is very small also in the liquid state. A rough estimate of the experimental error in the photographic photometry indicates that ΔH^{o} (liquid) < 300 cal/mole.

The absence of observable enthalpy differences between the "trans" and "gauche" isomers can be explained from steric considerations. According to Mizushima,[20] steric factors are largely responsible for the stability of the isomers. The steric repulsion should be nearly the same in the "trans" and the "gauche" forms. It should be quite small for all of these molecules, since the distances between non-bonded atoms are larger than, or of the same order as, the sum of the van der Waals' radii. Molecules for which a considerable enthalpy difference between the trans and gauche forms have been reported are mostly of the form $CH_2X - CH_2X$ or $CHX_2 - CHX_2$.[56] In these molecules a considerable repulsion is present in the gauche but not in the trans form, making the latter the more stable.

In molecules of the form $CH_2X - CH_2X$ (chapter IV) and $CHX_2 - CHX_2$ (chapter III) a considerable difference exists between the dipole moments of the trans and gauche forms. According to Onsager's theory of dielectrics,[43] the polar gauche form should be stabilized relative to the trans form on going from the gaseous to the liquid state. Because of the small difference between the moment of the C-F bond,

on the one hand, and the C-Cl and C-Br moments, on the other,[60] the $-CF_2Cl$ and $-CF_2Br$ end-groups will have a resulting dipole moment that is nearly parallel to the C-C bond. The "trans" and "gauche" forms of (C) and (B) will therefore have very similar dipole moments and hence should undergo about the same stabilization in the liquid state. The nearly equal values of ΔH^o in the gaseous and liquid states are therefore to be expected.

As has been mentioned, no bands present in the spectra of gaseous (C) and (B) disappear in the solid state. This is contrary to what has been found for several halogenated ethanes for which the disappearance of bands has been interpreted to mean that only one isomer is present in the solid state.[20] It must be concluded, therefore, that for (C) and (B) both isomers are present in the solid state. Similar results have been reported by Kagarise and Daasch for $CFCl_2 - CFCl_2$[29] and have been obtained in this laboratory for $CH_2F - CH_2F$ (chapter IV), $CF_2Cl - CFCl_2$ (chapter VI), $CF_2Br - CCl_2Br$ (chapter VII), $CF_2Br - CHBr_2$[13] and $CF_2Br - CFBr_2$.[21] The reason why some halogenated ethanes seem to exist as a mixture of rotational isomers in the solid state, while others exist as one isomer, only, is not known. A possible explanation is that the solids of the former are non-crystalline amorphous glasses having essentially the same spectra as the liquid. Malherbe and Bernstein[52] have reported that amorphous materials were sometimes formed

on the solidification of 1,2-dichloroethane. Kagarise and Daasch[29] also report that the existence of two isomers in the solid state of CF_2Cl - CF_2Cl may be due to an amorphous phase.

However, there are a number of reasons for believing that (C) and (B) are crystalline in the solid state.

1. When the samples were allowed to solidify under different conditions (slow, fast and at different temperatures) no significant differences were observed in their infrared spectra.
2. When the solid samples were allowed to warm up slowly, no change in the spectra was observed below the melting point. This is at variance with Malherbe and Bernstein's[52] report of a transition from the amorphous to crystalline phase below the melting point.
3. Visual examination of the samples at -180°C showed them to appear like crystalline aggregates.

It may be noted that most of the molecules that have been reported to crystallize as one isomer only, show significant enthalpy differences between the rotational isomers in the gaseous and liquid states. It is possible that molecules having very small enthalpy difference between the isomers may easily form a mixed crystal in the solid state. That other factors than the enthalpy difference in the

gaseous and liquid states are important for the crystalline state, however, is clearly shown by Kagarise's report that $CHBr_2$ - $CHBr_2$[61] will crystallize either as trans or gauche depending on the conditions.

Further studies of CF_2Cl - CHF_2 and CF_2Br - CHF_2 by other methods, such as electron diffraction, X-ray techniques or microwave spectroscopy, are necessary to fully determine the structure of their rotational isomers.

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[61] R. E. Kagarise, J. Chem. Phys. 24, 300 (1956).

TABLE X

INFRARED SPECTRAL DATA FOR $CF_2Cl - CHF_2$

Gas		Solid[a]		
Wave Number	Description[b]	Wave Number	Description[b]	Interpretation[c]
314	w			
321	m			fundamental I
		353	m	
358	w			fundamental I,II
		361	m	
389	w			2 x 196 = 392; 138 + 253 = 391
		412	vw	
426	m	426	m	196 + 231 = 427
431	m	431	s	fundamental I,II
437	m			
457	m	459	m	fundamental I,II
555				
561	vs	554	s	fundamental II
567		559	m	138 + 431 = 569
637	m	634	m	fundamental I,II
672				
678	vs	672	s	fundamental I,II
683				
732	vw			321 + 431 = 752
756	m			196 + 561 = 757
801	s	800	m	253 + 561 = 814

TABLE X--Continued

Gas		Solid[a]		
Wave Number	Description[b]	Wave Number	Description[b]	Interpretation[c]
809	s			138 + 678 = 816
826 833 839	vs	828	vs	fundamental I,II
		844	w	196 + 634 = 830
890	w	894	vw	253 + 637 = 890; 340 + 561 = 901
914 922 929	s	919	w	fundamental I,II
964	vw	971	vw	138 + 833 = 971; 340 + 637 = 977
992 999 1006	vs	996	vs	fundamental II
		1031	vw	358 + 672 = 1030
		1051	w	231 + 828 = 1059
1076 1082 1090	vs	1070	vs	fundamental I
1106	vw	1097	vw	431 + 678 = 1109
1125	m			138 + 999 = 1137; 457 + 678 = 1135

TABLE X--Continued

Gas		Solid[a]		
Wave Number	Description[b]	Wave Number	Description[b]	Interpretation[c]
1134 1142	vs	1116	vs	fundamental I
1161 1169 1175	vs	1153	vs	fundamental II
		1191	vw	358 + 833 = 1191; 196 + 999 = 1195
1214	vw	1212	s	fundamental I
1248 1255 1260	vs	1245	vs	fundamental II
		1263	w	196 + 1070 = 1266
1301	w			138 + 1169 = 1307
1312	s	1313	s	637 + 678 = 1315; 514 + 801 = 1315
1322	s			196 + 1138 = 1334
1344 1352 1356	s	1353	s	fundamental I
1386 1396 1402	vs	1391	s	fundamental II
1415	m			253 + 1169 = 1422
1448	m			196 + 1255 = 1451

TABLE X--Continued

Gas		Solid[a]		
Wave Number	Description[b]	Wave Number	Description[b]	Interpretation[c]
1526	w			138 + 1396 = 1534
1580	w			231 + 1352 = 1583
1649	m			253 + 1396 = 1649
1688	m			431 + 1255 = 1686
1751	w			358 + 1396 = 1754
1806	m			637 + 1169 = 1806
1831	w	1822	vw	833 + 999 = 1832
1890	w			637 + 1255 = 1892
1959	w			833 + 1134 = 1967
1991	vw			2 x 999 = 1998
2052	vw			922 + 1138 = 2060
2076	m	2062	vw	833 + 1255 = 2088
2155	m	2141	w	2 x 1082 = 2164
[2247][d]	s			999 + 1255 = 2254
[2273]	s			2 x 1138 = 2276
[2278]	s	2236?	m	1082 + 1214 = 2296
[2320]	m	2344?	m	2 x 1169 = 2338
[2381]	w			999 + 1396 = 2395
[2415]	w			1169 + 1255 = 2424
2489	w			1138 + 1352 = 2490
2496	w			2 x 1255 = 2510
2524	w			

TABLE X--Continued

Gas		Solid[a]		
Wave Number	Description[b]	Wave Number	Description[b]	Interpretation[c]
2561	w			1169 + 1396 = 2565
		2595	w	
2680	w	2671	vw	2 x 1352 = 2704
2746	w	2739	w	3001 - 253 = 2748
2775	w			2 x 1396 = 2792
2980				
2987	vs			fundamental I
2996				
3001	vs			fundamental II
3006				
3187	vvw			196 + 3001 = 3197
3245	vvw			253 + 3001 = 3254
3344	vvw			358 + 2987 = 3345
3394	vw			431 + 2987 = 3418
3822	vw			833 + 2987 = 3820
4072	w	4067	w	1082 + 2987 = 4069
4129	m	4117	w	1138 + 2987 = 4125
4198	vw			1214 + 2987 = 4201
4252	vw	4241	w	1255 + 3001 = 4256
4338	w	4325	w	1352 + 2987 = 4339
4403	m	4388	w	1396 + 3001 = 4397

[a]Solid film at -170°C. The thickness varied from record to record, but was not measured. Hence, the relative intensities indicated have less significance than for a gas. The solid state spectra were only recorded above 360 cm^{-1}.

[b]For the meaning of the abbreviations used, see footnotes to Table I.

[c]Roman numerals I and II refer to different rotational isomers.

[d]Frequencies enclosed in brackets were masked by strong carbon dioxide absorption, and has been taken from reference 58.

TABLE XI

INFRARED SPECTRAL DATA FOR $CF_2Br - CHF_2$

Gas		Solid[a]		
Wave Number	Description[b]	Wave Number	Description	Interpretation[c]
307	s			fundamental II
332	m			fundamental I,II
363	vw			fundamental I,II
389	w			554 - 165 = 389
412	w	412	w	718 - 307 = 411
434 438 442	s	440	w	fundamental I,II
513	m			fundamental I
		539	vw	182 + 365 = 547
549 554 559	vs	553	vs	fundamental II
577	m	576	vw	
		599	m	165 + 440 = 605
618	vs	614	vs	fundamental I
656	s	657	s	fundamental I,II
665	s	664	s	
710 718 725	s	710	s	fundamental I,II

TABLE XI--Continued

Gas		Solid[a]		
Wave Number	Description[b]	Wave Number	Description	Interpretation[c]
749	m			307 + 438 = 745
773	vw	780	w	332 + 438 = 770; 165 + 618 = 783
		790	w	182 + 614 = 796
		798	m	363 + 440 = 803
819 824 829	vs	819	vs	fundamental I,II
870	m	862	w	2 x 438 = 876; 363 + 513 = 876
896	s			182 + 718 = 900
		939	w	332 + 614 = 946
		955	m	440 + 513 = 953; 307 + 661 = 968
963 969 974	vs	967	vs	fundamental II
995	w	993	m	332 + 661 = 993; 182 + 824 = 1006
1029	w			2 x 513 = 1026; 307 + 718 = 1025
1035	vw	1037	w	332 + 718 = 1050
1062 1069 1076	vs	1056	vs	fundamental I

TABLE XI--Continued

Gas		Solid[a]		
Wave Number	Description[b]	Wave Number	Description	Interpretation[c]
		1081	m	440 + 661 = 1101
1135	vs	1115	vs	fundamental I
1164	vs	1152	vs	fundamental II
1207	vw	1203	s	fundamental I
1245	vs	1237	vs	fundamental II
1279	vw	1257	w	618 + 661 = 1279; 307 + 969 = 1276
1286	w	1277	m	165 + 1135 = 1300
		1309	vw	
1322	m	1320	w	165 + 1164 = 1329
1348	s	1348	s	fundamental I
1384	vs	1384	vs	fundamental II
1426	vw	1420	w	182 + 1245 = 1427
1499	vw			363 + 1135 = 1498
1535	w			718 + 824 = 1542; 165 + 1384 = 1549
1610	s	1603	m	363 + 1245 = 1608
1672	w			332 + 1348 = 1680
1679	w			438 + 1245 = 1683
1793	m	1793	w	661 + 1135 = 1796
1829	m	1815	w	661 + 1164 = 1825
1869	w	1867	vw	718 + 1164 = 1882
1908	vw			718 + 1207 = 1925

TABLE XI--Continued

Gas		Solid[a]		
Wave Number	Description[b]	Wave Number	Description	Interpretation[c]
1944	m	1939	vw	2 x 969 = 1938
1960	w			824 + 1135 = 1959
1968	w			618 + 1348 = 1966
1979	w			824 + 1164 = 1988
2014	vw			661 + 1384 = 2045
2060	m			718 + 1348 = 2066
2069	vw			824 + 1245 = 2069
2130	m	2112	w	2 x 1069 = 2138; 969 + 1164 = 2133
2212	s			1069 + 1135 = 2204
2228	s	2244	m	969 + 1245 = 2214
2271	s	2257	vw	2 x 1135 = 2270
2277	m			1069 + 1207 = 2276
2304	s			2 x 1164 = 2328
2340	w			1135 + 1207 = 2342
2366	m			969 + 1384 = 2353
2408	m			2 x 1207 = 2414; 1164 + 1245 = 2409
2461	w			1135 + 1348 = 2483
2485	m			2 x 1245 = 2490
2490	vw			
2514	w	2514	vw	1164 + 1384 = 2512
2552	m			1207 + 1348 = 2555

TABLE XI--Continued

Gas		Solid[a]		
Wave Number	Description[b]	Wave Number	Description	Interpretation[c]
2590	vw	2583	vw	
2632	w	2619	vw	2998 - 363 = 2635
2674	m	2671	vw	2998 - 332 = 2666
2681	w			2 x 1348 = 2696
2735	w	2731	w	
2762	w			2 x 1384 = 2786
2818	w			2977 - 165 = 2812
2927	w			
2977	vs	2987	s	fundamental I
2998	vs			fundamental II
3061	vw			
3245	vw			
3322	vw			332 + 2998 = 3330
3374	vw			363 + 2998 = 3361
3412	vw			438 + 2977 = 3415
3597	w			618 + 2977 = 3595
3820	w			824 + 2998 = 3822
4049	m	4044	vw	1069 + 2977 = 4046
4117	m	4105	vw	1135 + 2977 = 4112
4134	w			
4172	w	4184	vw	1207 + 2977 = 4184

TABLE XI--Continued

Gas		Solid[a]		
Wave Number	Description[b]	Wave Number	Description	Interpretation[c]
4239	vw			1245 + 2998 = 4243
4330	w	4323	vw	1348 + 2977 = 4325
4367	m	4374	vw	1384 + 2998 = 4382
5618	w			
5714	w			

[a]See footnote a, Table X.

[b]For abbreviations used see footnotes to Table I.

[c]For meaning of I and II see footnote c, Table X.

TABLE XII

RAMAN SPECTRAL DATA FOR LIQUID $CF_2Cl - CHF_2$

Wave Number	Description[a]	Depolarization[b]	Exciting Hg lines[c]	Interpretation[d]
[93.0?][e]				
ca138*	vw		±e	fundamental I,II
ca196	w		±e	fundamental I,II
231*	vvw		e	fundamental I
253	w		e,k	fundamental II
321	s,sh	0.5	±e,k,i	fundamental I
340	m	0.7	±e,k	fundamental II
361	s,sh	0.6	±e,k	fundamental I,II
432	vs,b	0.3	±e,k,i	fundamental I,II
458	s	0.5	e,k	fundamental I,II
496*	w,d	0.8	e	138 + 361 = 499; 2 x 253 = 506
514	w,d	0.8	e	196 + 321 = 517
560	m,sh	0.5	e,k	fundamental II
638	vs,sh	0.1	e,k	fundamental I,II
672	vs,b	0.1	e,k	fundamental I,II
699	w		e	340 + 361 = 701
720*	vw		e	2 x 361 = 722
828	s	0.2	e,k	fundamental I,II
863*	vw		e	2 x 432 = 864
[910.2]				
995	w,d	0.9	e	fundamental II

TABLE XII--Continue

Wave Number	Description[a]	Depolarization[b]	Excit Hg 1: [c]	Interpretation[d]
1072	m,d	0.6	e,k	fundamental I
1115	m	0.5	e	fundamental I
1145	m	0.5	e	fundamental II
1214	m		e	fundamental I
1249*	w,d		e	fundamental II
1318*	vw		e	253 + 1072 = 1325
1358	m,d	0.9	e	fundamental I
1399*	w,d	0.5	e	fundamental II
2980-3015	vs	0.2	e,k,i	fundamental I,II

[a]For the meaning of the abbreviations used see footnotes to Table II.

[b]Measured depolarization ratios.

[c]See footnote b, Table II for the meaning of the Kohlrausch symbols.

[d]Roman numerals I and II refer to different rotational isomers.

[e]Bands enclosed by brackets were observed by Glockler and Sage (ref. 57) but not in the present work.

*Bands with an asterisk have not been observed by Glockler and Sage (ref. 57).

TABLE XIII

RAMAN SPECTRAL DATA FOR LIQUID $CF_2Br - CHF_2$

Wave Number	Description[a]	Depolarization[b]	Exciting Hg lines[c]	Interpretation[d]
ca165	w		±e	fundamental I,II
ca182	w	p	±e	fundamental I,II
299	s,sh	0.8	±e,k,i	fundamental I
312	s,sh	0.3	±e,k,i	fundamental II
331	vs,b	0.3	±e,k,i	fundamental I,II
365	s,sh	0.1	e,h	fundamental I,II
439	w	0.5	e,k	fundamental I,II
504	w,d	0.8	e	182 + 331 = 513 I
554	s	0.2	e,k	fundamental II
600	vvw		e	165 + 439 = 604
614	vs	0.1	e,k	fundamental I
623	vs	0.1	e,k	fundamental II
665	s,sh	0.15	e,k	fundamental I,II
711	w		e	fundamental I,II
770	vvw		e	331 + 439 = 770
819	s	0.12	e,k,i	fundamental I,II
861	vw		e	312 + 554 = 866
906	w	0.5	e	299 + 614 = 913
955	w	0.3	e	299 + 665 = 964
967	m		e,k	fundamental II
1061	s	0.3	e,k	fundamental I
1104	m,d	0.3	e,k	fundamental I

TABLE XIII--Continued

Wave Number	Description[a]	Depolarization[b]	Exciting Hg lines[c]	Interpretation[d]
1134	m,d	0.3	e,k	fundamental II
1205	m		e,k	fundamental I
1238	w,d		e	fundamental II
1279	vw		e	182 + 1104 = 1286
1349	s	0.8	e,k	fundamental I
1386	m	0.3	e,k	fundamental II
1422	w,d		e	2 x 711 = 1422
1775	vw,d		e	439 + 1349 = 1788; 711 + 1061 = 1772
2970-3010	s	0.19	e,k,i	fundamental I,II

[a]For abbreviations used see footnote a in Table XII.

[b]Numbers indicate the measured depolarization ratios: p polarized, d depolarized.

[c]See footnote b, Table II for the meaning of the Kohlrausch symbols.

[d]Roman numerals I and II refer to different rotational isomers.

TABLE XIV

FUNDAMENTAL VIBRATIONAL FREQUENCIES FOR
$CF_2Cl - CHF_2$ AND $CF_2Br - CHF_2$

$CF_2Cl - CHF_2$			$CF_2Br - CHF_2$			Approximate[a] Motion
Infrared		Raman	Infrared		Raman	
Gas	Solid[b]	Liquid	Gas	Solid[b]	Liquid	
		138w[c]				Torsional I,II
		196w			165w	Rocking I,II
		231vw				Rocking I
					182w	Rocking I,II
		253w				Rocking II
321m		321s			299s	Rocking I
		340m	307s		312s	Rocking II
358w	353m 360m	361m	332m		331vs	Rocking I,II
431s	431s	432vs	363vw		365s	CF_2Hal bend I,II
457m	459m	458s	438s	440w	439m	CF_2Hal bend I,II
		514w	513m		504m	CHF_2 bend I
561vs	554s	560m	554vs	553vs	554m	CHF_2 bend II
637m	634m	638s				CF_2Hal bend I,II
			618vs	614vs	614vs	CF_2Hal bend I
					623vs	CF_2Hal bend II
678vs	672s	672s	656s 665s	657s 664s	665vs	C-Hal stretch I,II
801m	800m		718vs	710s	711vw	CH_2F bend I,II
833vs	828vs	828vs	824vs	819vs	819s	C-C stretch I,II

TABLE XIV--Continued

$CF_2Cl - CHF_2$			$CF_2Br - CHF_2$			Approximate[a] Motion
Infrared		Raman	Infrared		Raman	
Gas	Solid[b]	Liquid	Gas	Solid[b]	Liquid	
922s	919w		870m	862w	861w	C-F stretch I,II
999vs	996vs	995w	969vs	967vs	967m	C-F stretch II
1082vs	1070vs	1072w	1069vs	1056vs	1061s	C-F stretch I
1138vs	1116vs	1115m	1135vs	1115vs	1104s	C-F stretch I
1169vs	1153vs	1145m	1164vs	1152vs	1134s	C-F stretch II
1214vw	1212s	1214m	1207vw	1203s	1205m	CHF_2 deform I
1255vs	1245vs	1249m	1245vs	1237vs	1238w	CHF_2 deform II
1352s	1353s	1358m	1348s	1348s	1349s	C-F stretch I
1396vs	1391s	1399vw	1384vs	1384vs	1386m	C-F stretch II
2987vs	2999s	2997vs	2977vs	2987s	2990s	C-H stretch I
3001vs	2999s	2997vs	2998vs	2987s	2990s	C-H stretch II

[a]Roman numerals I and II refer to different rotational isomers.

[b]See footnote a, Table X.

[c]See footnote b, Table X for abbreviations used.

CHAPTER VI

INFRARED AND RAMAN SPECTRA OF $CF_2Cl - CFCl_2$

Introduction

The vibrational spectra of a number of halogenated ethanes with asymmetrical end-group, CX_2Y, have been studied by different authors.[20,26,29,38] The Raman[57] and infrared[62] spectra of liquid $CF_2Cl - CFCl_2$ have been observed but no attempts to assign the fundamentals or study the relative stabilities of the rotational isomers have been reported. In the present paper new infrared and Raman spectral data for $CF_2Cl - CFCl_2$ are reported, and the rotational isomerism exhibited by this compound is studied. The slight intensity variations observed with changing temperature of certain infrared and Raman bands have been used to distinguish between the vibrational fundamentals of different isomeric forms. However, for several fundamentals, particularly for those represented by weak or medium intensity bands, this was not possible, and more uncertain criteria had to be used. A tentative, and in part rather uncertain, assignment of the

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NRL Report No. 3567. Spectroscopic Properties of Fluorocarbons and Fluorinated Hydrocarbons (Naval Research Laboratory, Washington D.C., 1949).

fundamentals belonging to each isomer has been made, and the spectra have been interpreted in detail.

Experimental Results

The sample of $CF_2Cl - CFCl_2$ (bp 43°C at 760 mm) was prepared by Professor J. D. Park at the University of Colorado. The spectra indicate that the purity is high, except for the presence of a small amount of carbon dioxide. The infrared absorption spectrum of the gas at room temperature was recorded with the aid of a Perkin-Elmer Model 112 spectrometer equipped with CsBr, NaCl and LiF prisms and 6-cm, 10-cm and 1-m cells. To study the rotational isomerism, the infrared spectrum of the gas in an electrically heated 10-cm cell[13] was obtained also at 50°, 70°, 90° and 110°C. Since the infrared spectrum of the liquid was available,[62] no complete redetermination of this spectrum was carried out. However, the spectral region from 650 to 1400 cm^{-1} was studied with the sample dissolved in different solvents, ranging from the non-polar carbon tetrachloride to the strongly polar nitromethane. The infrared spectrum of the solid at -180°C was obtained by means of a low temperature cell.[13] The Raman spectrum of the liquid, contained in a sealed Pyrex tube was photographed with an Applied Research Laboratories 3-prism glass spectrograph of reciprocal linear dispersion 15 A/mm at 4358A. Raman spectra of the liquid at low temperatures were obtained by the method described by Jackson.[37] Identical sets of exposures were made at 30° and -40°C, and the

intensities of the bands were compared by means of a microphotometer. Because of experimental difficulties in obtaining reliable data from the very small sample available, depolarization measurements were not made. Depolarization data would have been of limited value anyway, since one of the rotational isomers has no symmetry element, and since there is a considerable amount of overlapping of Raman bands belonging to different isomers. The infrared spectrum of the gas is shown in Figs. 27-29, and the wave numbers of the observed absorption maxima (or "shoulders") are listed in Table XV. The Raman spectral data are presented in Table XVI. All the bands reported by Glockler and Sage[57] were observed, and two additional weak bands, including a very weak band at ca 80 cm^{-1}.

Interpretation

The large amount of information available about ethane and halogen-substituted ethanes indicates that these molecules exist in staggered configurations only. The eclipsed configurations have not been observed and are probably energetically unstable. The large number of infrared and Raman bands observed in the spectra of $CF_2Cl - CFCl_2$ suggests strongly that this compound exists as a mixture of rotational isomers. This conclusion was also reached by Glockler and Sage.[57] The probable isomeric configurations are a form having the symmetry C_s and a form obtained from this by rotating one of the end-groups a certain angle,

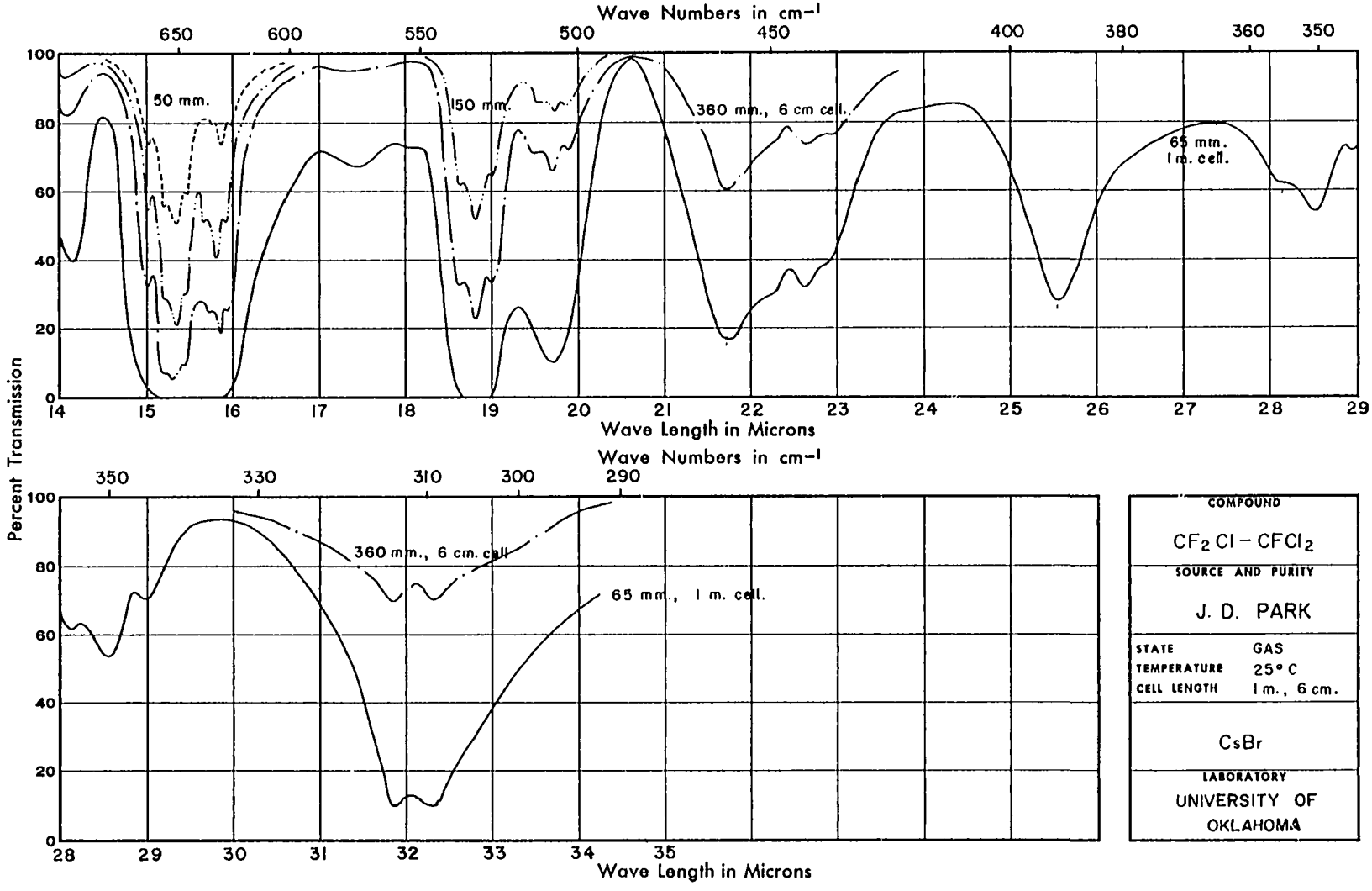

Fig. 27. Infrared Spectrum of Gaseous $CFCl_2$ -CF_2Cl (CsBr Region)

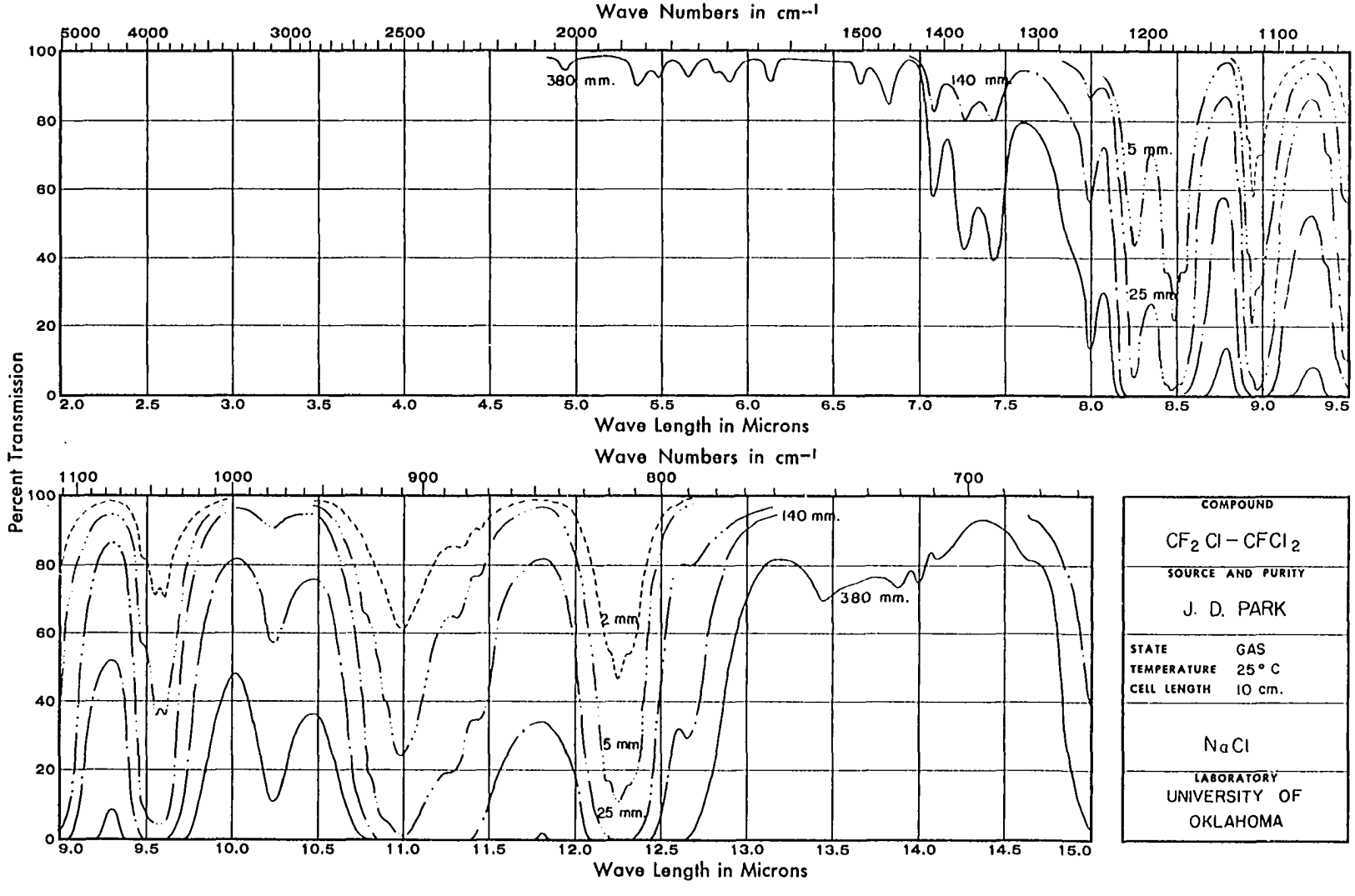

Fig. 28. Infrared Spectrum of Gaseous CF_2Cl-$CFCl_2$ (NaCl Region)

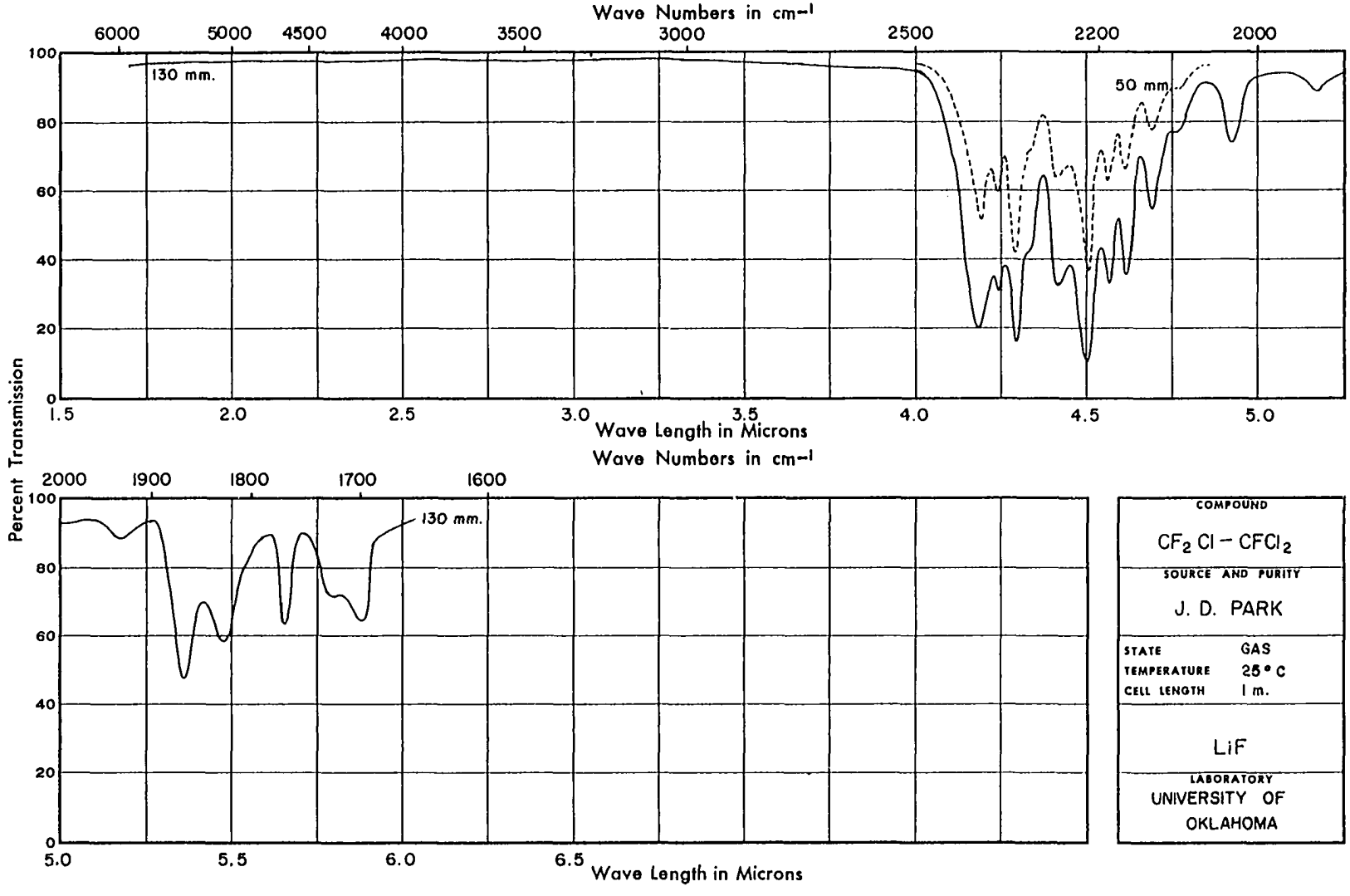

Fig. 29. Infrared Spectrum of Gaseous CF_2Cl-$CFCl_2$ (LiF Region)

probably close to 120°. The latter form has no symmetry, i.e. belongs to the point group C_1. These two forms will be referred to in what follows as the "trans" and "gauche" forms, respectively.

The 18 normal vibrations of the "trans" form divide into 11 a' and 7 a". The former should be polarized in the Raman spectrum, while the latter should be depolarized. The vibrations of the "gauche" form all belong to the same species a. All fundamentals belonging to either isomer are active in both spectra. Assuming the interatomic distances C-C = 1.54, C-F = 1.37, C-Cl = 1.77A, and tetrahedral angles, one finds the following principal moments of inertia for the "trans" form: 609.0, 815.2 and 770.7 x 10^{-40} gcm^2. The axis of smallest and largest moments of inertia lie in the symmetry plane, the latter axis making an angle of 85°43' with the C-C bond. Infrared bands of species a" should therefore have type B contours in the spectrum of the gas, while bands of species a' should have contours that are hybrids between A and C. Extrapolation from Badger and Zumwalt's curves[39] gives QQ and PR separations of 1.3 and 11 cm^{-1} for type B bands and PR separations of 10 and 13 cm^{-1} for type A and type C bands, respectively. If one considers the "trans" molecule as approximately a symmetrical top, interpolation from Gerhard and Dennison's curves[54] gives PR separations 10 and 11 cm^{-1} for parallel and perpendicular bands, respectively. It follows from these results that the infrared

contours are not very useful for assigning the fundamentals of the "trans" isomer. For the "gauche" isomer no predictions can be made about the contours.

No completely reliable method was found to determine which of the observed fundamentals belong to the "trans" form, which belong to the "gauche" form and which are common to both isomers. None of the strong infrared bands of the gas or liquid disappears in the spectrum of the solid. The intensity variations with temperature of some infrared and Raman bands observed in the gas and liquid, respectively, were very small and gave useful information only in some cases. Moreover, no significant relative intensity variation of the strong infrared bands in the region from 650 to 1300 cm^{-1} was found when the compound was dissolved in solvents of different dielectric constants. The observed infrared combination bands should give some information about which fundamentals belong to the same isomeric form. However, because of the large number of fundamentals the interpretation of the combination bands is in many cases not unique. It was found that the observed combination bands were of value mainly for the assignments of the fundamentals lying in the region from 900 to 1300 cm^{-1}. In view of all of these facts, the assignments of fundamentals of each isomer given separately below must be regarded as tentative.

Since the present compound contains only carbon,

fluorine and chlorine atoms, fairly reliable predictions can be made about the number of fundamentals expected in the different frequency regions. In the region from 1300 to 1000 cm^{-1} three fundamentals of each isomer involving C-F stretching are expected. Actually, 6 strong bands are observed in this region. Furthermore, all of these bands have the characteristic appearance of the C-F stretching vibrations,[14] i.e. they are weak and diffuse in the Raman spectrum and very strong in the infrared. In addition, there is in this region a very close similarity with the infrared and Raman spectra of CF_2Br - $CFBr_2$ which recently have been obtained in this laboratory.[21] The slight intensity variations with temperature observed for some of these bands in the infrared, as well as the position of overtones in the region 1900 - 2400 cm^{-1} have been used as clues to their assignment. With the exception of the strong Raman band at 1046 cm^{-1} and the medium band at 1209 cm^{-1} which both decrease in intensity with increasing temperature, the Raman bands in this region are too weak to exhibit any detectable intensity variation. The infrared bands at 1114 and 1041 cm^{-1} seem to be enhanced relative to the bands at 1119 and 1047 cm^{-1} as the temperature is raised. Possible variations of the infrared bands at 1212 and 1179 cm^{-1} were masked by absorption caused by decomposition products, to be discussed later. These bands are undoubtedly all fundamentals. In view of their temperature behavior, the

fundamentals at 1047, 1119 and 1212 cm^{-1} (in the infrared spectrum of the gas) will be ascribed to one rotational isomer for which the non-committal designation I will be used, and the fundamentals at 1041 and 1114 cm^{-1} will be ascribed to the other isomer, designated II. The very strong infrared band at 1179 cm^{-1}, and its counterpart in the Raman spectrum of the liquid at 1169 cm^{-1}, is assigned as a fundamental of II.

These assignments give a more satisfactory interpretation of the weak bands in the region 1900 to 2500 cm^{-1} than any other assignments considered. The weak infrared band at 2386 cm^{-1} presents a problem. If the fundamentals at 1179 and 1212 cm^{-1} were ascribed to the same isomer, this band could readily be explained as their combination. However, this does not seem reasonable. It is assumed, therefore, that the band at 2386 cm^{-1} is a ternary combination band. Since there are several such combinations possible, none is listed in Table XV.

The very strong infrared band at 909 cm^{-1} and the weak Raman band at 902 cm^{-1} undoubtedly represent a fundamental associated largely with C-C stretching. This fundamental is somewhat arbitrarily ascribed to I. The corresponding fundamental of II is assumed to be represented by the very weak infrared band observed near 927 cm^{-1} in both the gas and the liquid[62] and by a very weak Raman band at the same spectral position. This assignment is rather

uncertain, since the bands at 927 cm^{-1} could also be interpreted as a binary combination. If this alternative were adopted, it would be necessary to assume that fundamentals I and II overlap at 909 cm^{-1}.

In the region from about 600 to 900 cm^{-1} one would expect 3 fundamentals of each isomer involving C-Cl stretching. However, only three strong bands have been found in the infrared and two in the Raman spectrum in this region. The infrared band at 816 cm^{-1} with a PR separation of 9 cm^{-1} is the strongest in the entire spectrum. Its intensity shows no temperature variation, and it is therefore interpreted as overlapping fundamentals of I and II. It is surprising that no corresponding Raman band was observed, since vibrations involving C-Cl stretching usually are rather strong in the Raman spectrum. The strong infrared bands at 651 and 632 cm^{-1}, having PR separations 9 and 11 cm^{-1}, respectively, correspond to the sharp Raman bands at 652 and 631 cm^{-1}, of which the former is very strong and the latter of medium intensity. Because of their sharpness it is assumed that each of these bands belongs to one isomer only. There is a slight indication of an increase in intensity of the Raman band at 652 cm^{-1} with increasing temperature. This band and the corresponding infrared band are assigned as a fundamental of II and the bands near 632 cm^{-1} as a fundamental of I.

The strong infrared band, with PR separation 10 cm^{-1},

and the medium intense, sharp Raman band at 531 cm^{-1} both decrease in relative intensity with increasing temperature. They are interpreted as a fundamental of I. On the other hand, the similar bands at 507 cm^{-1} which are enhanced as the temperature is raised, are assigned as a fundamental of II. Since the wave numbers of these bands are some 100 cm^{-1} lower than what would be expected for pure C-Cl stretching, the vibrations associated with them must be rather complex.

It is interesting to compare these bands with the corresponding bands of $CF_2Br - CFBr_2$.[21] This compound has a very strong infrared band at 681 cm^{-1} with no counterpart in the Raman spectrum, as well as bands near 662, 643 and 600 cm^{-1} present in both spectra. Evidently, the highest of these fundamentals for the rotational isomers of $CF_2Br - CFBr_2$ overlap and are observed only in the infrared spectrum, whereas the other fundamentals appear as separate bands for each isomer, just as for $CF_2Cl - CFCl_2$. In $CF_2Br - CFBr_2$, however, these fundamentals lie in the expected spectral region. Thus, it appears that C-Br stretching is less susceptible to coupling with other vibrations than C-Cl stretching. This has been observed in other cases.[63]

Below 500 cm^{-1} the fundamentals associated with deformations of the CF_2Cl and $CFCl_2$ groups and with rocking and torsion are expected, or 11 fundamentals for each isomer.

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[63]L. J. Bellamy, The Infra-red Spectra of Complex Molecules, p. 269 (Methuen and Co. Ltd., London, 1954).

Since only 15 Raman bands and ca 10 infrared bands strong enough to be considered as fundamentals have been observed in this region, the majority of these bands must be interpreted as overlapping fundamentals of I and II.

The strong, broad Raman band at 458 cm^{-1} and the medium infrared bands at 460 cm^{-1} in the gas and at 461 and 457 cm^{-1} in the solid undoubtedly represent a pair of fundamentals of I and II. The very strong and medium intensity Raman bands at 441 and 438 cm^{-1}, respectively, and the infrared bands at nearly the same wave numbers, are interpreted as another pair of fundamentals of I and II.

The diffuse Raman bands at 392 and 373 cm^{-1} are each assigned as a pair of fundamentals of I and II. In the infrared spectrum of the gas the former of these pairs is observed as a single absorption maximum and the second pair is not observed. In the infrared spectrum of the solid, on the other hand, these fundamentals seem to appear separately at 395 and 391 and at 380 and 374 cm^{-1}. It does not seem possible to decide which of these belong to I and which to II, especially since this problem is complicated by the fact that two of these solid state bands could be interpreted as combination bands.

The weak infrared band at 350 cm^{-1} of uncertain contour is assigned as overlapping fundamentals of I and II, in spite of the fact that the counterpart in the Raman spectrum appears to be quite sharp. The two closely spaced

infrared absorption maxima at 314 and 309 cm^{-1} undoubtedly represent separate bands corresponding to the somewhat more widely separated Raman bands at 316 and 305 cm^{-1} in the liquid. No observations on intensity variations with temperature could be made. The bands of higher wave number is arbitrarily interpreted as a fundamental of II and those of lower wave number as a fundamental of I. All of the fundamentals between 500 and 300 cm^{-1} are associated largely with deformations of the CF_2Cl and $CFCl_2$ groups.

The 7 Raman bands observed below 300 cm^{-1} are undoubtedly all fundamentals. The strong Raman band at 288 cm^{-1} is assigned as overlapping fundamentals of I and II, in spite of the fact that a small decrease in intensity with increasing temperature appeared to occur. The weak Raman band at 251 cm^{-1} and the strong band at 240 cm^{-1} are interpreted as fundamentals of II and I, respectively. The band at 203 cm^{-1} is ascribed to both I and II, and the bands at 183 and 168 cm^{-1} are assumed to be fundamentals of II and I, respectively. The four fundamentals (for each isomer) just mentioned involve largely rocking motions. The lowest Raman band, at ca 80 cm^{-1}, is interpreted as overlapping fundamentals of I and II associated with torsion. It corresponds to a band at 59 cm^{-1} in the Raman spectrum of $CF_2Br - CFBr_2$.[21]

The assigned fundamentals for isomer I and II are listed in Tables XVII and XVIII, respectively. The

assignment of the bands to a definite isomer should be considered tentative, especially in the low-frequency region. A test of the assignments made is provided by the sum rule derived by Mizushima et al.[40] One obtains $\sum_i \nu_i^2 = 7{,}125 \times 10^3$ and $\sum_i \nu_i^2 = 7{,}071 \times 10^3$ for isomers I and II, respectively, i.e. within less than 0.8% of the same result. The empirical sum rule of Bernstein and Pullin[41] is satisfied even more precisely, the sums being $\sum_i \nu_i = 9{,}571$ and $\sum_i \nu_i = 9{,}576$ for isomers I and II, respectively.

As will be discussed later, there is some reason to assume that isomer II is "trans" and I is "gauche." However, since this is not certain, no species designations have been included in Tables XVII or XVIII which would correlate definately II and I with "trans" and "gauche."

In terms of the assigned fundamentals it has been possible to interpret all of the observed Raman bands and practically all of the infrared bands. These interpretations are given in Tables XV and XVI for the infrared and Raman bands, respectively. The infrared bands that have been left uninterpreted can be explained as ternary combination bands. However, in view of the large number of fundamentals, such interpretations are in most cases not unique and have therefore not been included.

Enthalpy Difference Between the Rotational Isomers

It has been mentioned that an intensity change of some of the infrared bands was observed when the gaseous

sample was heated from 30° to 110°C. The increases and decreases in the intensities are quite small, however, and the effect is nearly masked by experimental uncertainties. The measurements were made difficult by the fact that the molecule is not stable towards heating but decomposes quite fast above 130°C. Strong infrared bands belonging to the decomposition products appeared at 1729, 1198 and 1170 cm^{-1}, indicating the formation of an ethylene. Comparison with published infrared spectra shows that the decomposition products are neither $CCl_2 = CFCl$[64] nor $CF_2 = CFCl$.[62]

Peak extinctions of the following infrared bands were measured at different temperatures,

I 1119, 1047, 531

II 1114, 1041, 507,

and the graphical method of Bernstein[42] was used, corrections being made for a slight change of the zero transmission line with changing temperature. The following standard enthalpy difference between the isomers in the gaseous state was obtained: $\Delta H^{\circ} = 350 \pm 150$ cal/mole.

The Raman exposures of the liquid made at 30° and -40°C revealed intensity changes with temperature of some of the Raman bands. However, the photographic intensity data were not accurate enough to determine ΔH°. It was found that corresponding infrared and Raman bands showed qualitatively the same intensity variation with temperature in all

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[64]J. Rud Nielsen, C. W. Gullikson and A. H. Woollett, J. Chem. Phys. 23, 1994 (1955).

cases where a variation could be observed. Thus, the infrared bands at 1212 and 1047 cm^{-1} as well as the corresponding Raman bands at 1209 and 1046 cm^{-1} are reduced in intensity as the temperature is increased, while the infrared band at 507 and the Raman band at 506 cm^{-1} are both enhanced. One must conclude, therefore, that the same isomeric form is the more stable in both gas and liquid. This is not surprising, and there are good reasons for believing that the value of the enthalpy difference ΔH^{o} is nearly equal in the two states of aggregation. The bond moments for the C-F and the C-Cl bonds are 1.41 and 1.46 D, respectively.[60] The "trans" and "gauche" forms should therefore have nearly the same dipole moments. According to Onsager's theory[43] both isomers should undergo approximately the same changes in enthalpy when transferred from vacuum ($\varepsilon = 1$) to a medium of dielectric constant ε. This conclusion is supported by the measurements made when the compound was dissolved in different solvents of very low or very high dielectric constants; carbon tetrachloride and carbon disulphide or acetonitrile and nitromethane. This method, which has been used in many cases to displace the equilibrium between isomers[18,20,28] gave no positive results for this compound. The relative intensities of the strong infrared bands between 1250 and 800 cm^{-1} were measured when the compound was dissolved in the four solvents mentioned, but no variations were detected. Some of the bands, particularly that at 1171 cm^{-1}, became broader and of

smaller peak extinction in the polar solvents, but the integrated absorbance was nearly unchanged.

No significant change was found between the infrared spectra of the gas and liquid and the spectrum of the solid. It must be concluded, therefore, that both isomeric forms are present also in the solid state. A similar result was reported by Kagarise and Daasch for $CFCl_2$ - $CFCl_2$,[29] and a similar behavior upon solidification has been found here for CH_2F - CH_2F, CF_2Cl - CHF_2 and CF_2Br - CHF_2 (chapters IV and V). It is quite significant that also CF_2Br - $CFBr_2$,[21] behaves similarly on solidification. It is not known with certainty if the two isomers form a mixed crystal in the solid state or if an amorphous glass is formed. The existence of amorphous material formed upon solidification has been reported by Malherbe and Bernstein[52] and others. However, there are reasons to believe that the solid formed of the present compound was crystalline; for essentially the same spectrum was obtained under different conditions of solidification.

According to Mizushima[20] steric effects are largely responsible for the relative stabilities of the rotational isomers of halogenated ethanes in the gaseous state. It seems very likely that the "gauche" form should be more stable than the "trans" form for the present molecule, since steric repulsions between the chlorine atoms as well as electrostatic effects between the highly electronegative

fluorine atoms should favor the "gauche" form. It is surprising that a very small enthalpy difference between the isomers was found in the gas.

If the more stable isomer (I) is the "gauche" and the less stable (II) is the "trans," we would expect the "gauche" isomer to be considerably more abundant than the "trans" in the gas and liquid, since there are two enantiomorphic "gauche" forms but only one "trans" form. The intensities of the infrared and Raman bands assigned to one isomer are on the average, not very different from those assigned to the other. However, no reliable conclusions can be drawn from the absolute intensities of the infrared and Raman bands, because the extinction coefficients may vary widely from one isomer to the other.

TABLE XV

INFRARED SPECTRAL DATA FOR $CF_2Cl - CFCl_2$

Gas		Liquid[a]		Solid[b]		
Wave Number	Description[c]	Wave Number	Description[c]	Wave Number	Description[c]	Interpretation
309	m					fundamental I
314	m					fundamental II
344, 350, 355	w			351	w	fundamental I,II
				374	vvw	fundamental I
				380	w	fundamental II
391	m			391	w	fundamental I
				395	m	fundamental II
437	vw			437	vw	fundamental II
442	w	ca 444	w	444	m	fundamental I
448	vvw					203 + 251 = 454 II
				457	w	fundamental II
460	m	ca 461	m	461	m	fundamental I
503, 507, 512	m	509	m	507	w	fundamental II
526, 531, 536	s	532	m	530	s	fundamental I

TABLE XV--Continued

Gas		Liquid[a]		Solid[b]		
Wave Number	Description[c]	Wave Number	Description[c]	Wave Number	Description[c]	Interpretation
574	vw	561	vw			2 x 288 = 576 I,II; 183 + 392 = 575
626, 632, 637	s	633	s	629	s	fundamental I
647, 651, 656	s	653	s	650	s	fundamental II
683	vvw					240 + 442 = 682 I; 183 + 507 = 690 II
708	w					203 + 507 = 710 II
714	w	712	m	710	vw	ca80 + 632 = 712 I; 251 + 460 = 711 II
720	w					288 + 442 = 730 II
		ca 734	vw			203 + 532 = 735 I
744	w	ca 746	w			288 + 460 = 748 I,II
				782	vw	391 x 2 = 782 I,II
790	w	ca 789	w	789	m	350 + 442 = 792 I,II
811, 816, 820	vs	ca 806	vs	807	vs	fundamental I,II
		852	w	850	m	203 + 653 = 856 II
				854	m	351 + 507 = 858 II

TABLE XV--Continued

Gas		Liquid[a]		Solid[b]		
Wave Number	Description[c]	Wave Number	Description[c]	Wave Number	Description[c]	Interpretation
876	w	873	m	874	s	350 + 531 = 881 I
886	m	ca 886	m	887	s	2 x 442 = 884 I
909	vs	ca 902	vs	900	vs	fundamental I
918	vw			906	m	288 + 632 = 920 I; 2 x 460 = 920 I,II
927	vw	ca 924	w	927	s	fundamental II
976	s	971	s	972	w	350 + 632 = 982 I; 168 + 816 = 984 II
1041	vs	1033	vs	1031	vs	fundamental II
1047	vs	1045	vs	1042	vs	fundamental I
1056	vw			1061	w	240 + 816 = 1056 I; 2 x 531 = 1062 I
				1074	vvw	629 + 444 = 1073 I
1114	s			1087	s	fundamental II
1119	vs	1109	vs	1099	vs	fundamental I
1123	s					ca80 + 1047 = ca1127 I
				1136	vw	240 + 900 = 1140 I
1174						
1179	vs	1171	vs	1164	vs	fundamental II
1185				1185	w	288 + 900 = 1188 I
1212	vs	1209	vs	1209	s	fundamental I
1250	s	1248	m	1252	w	203 + 1047 = 1250 I; 350 + 909 = 1259 I

TABLE XV--Continued

Gas		Liquid[a]		Solid[b]		
Wave Number	Description[c]	Wave Number	Description[c]	Wave Number	Description[c]	Interpretation
1276	w					460 + 816 = 1276 I,II; 350 + 927 = 1277 II
		1307	w			203 + 1114 = 1317 II; 392 + 927 = 1319 II
1349	m	1342	m			442 + 909 = 1351 I
1378	m	1377	m			203 + 1179 = 1382 II; 168 + 1212 = 1380 I
1413	w	1414	w			203 + 1212 = 1415 I
1470	w	1458	w			437 + 1041 = 1478 II; 651 + 816 = 1467 I
1502	w	1490	w			460 + 1047 = 1507 I
		1527	vw			633 + 902 = 1535 I
		1567	vw			461 + 1109 = 1570 I
1642	w	1637	w			531 + 1119 = 1650 I; 460 + 1179 = 1639 II
1699	w	1700	w			651 + 1041 = 1692 II
1730	vw	1720	w			531 + 1212 = 1743 I; 816 + 927 = 1743 II
1767	w	1765	w			651 + 1114 = 1765 II
1822	w	1820	w			651 + 1179 = 1830 II; 2 x 909 = 1818 I
1863	w	1855	w			816 + 1041 = 1857 II
1933	vvw	1915	vw			816 + 1119 = 1935 I
2029	vw	2020	vw			816 + 1212 = 2028 I; 909 + 1119 = 2028 I

TABLE XV--Continued

Gas		Liquid[a]		Solid[b]		
Wave Number	Description[c]	Wave Number	Description[c]	Wave Number	Description[c]	Interpretation
2128	w	2120	vw			909 + 1212 = 2121 I
2165	w	2160	w			1047 + 1119 = 2166 I
2190	w					1041 + 1179 = 2220 II
2221	w	2215	w			2 x 1114 = 2228 II
2263	w					1047 + 1212 = 2259 I
2295	vw					1114 + 1179 = 2293 II
2328	w	2320	w			1119 + 1212 = 2331 I
2355	vw					2 x 1179 = 2358 II
2386	w	2380	w			
		ca3260	vvw			
		ca3420	vvw			

[a]The infrared bands in the liquid state obtained from ref. 62.

[b]The solid spectrum was only recorded in the region from 350 cm^{-1} to 1500 cm^{-1}.

[c]For the meaning of the abbreviations used see footnotes to Table I.

TABLE XVI

RAMAN SPECTRAL DATA FOR LIQUID CF_2Cl- $CFCl_2$

Wave Number	Description[a]	Exciting Hg lines[b]	Interpretation
ca80*	vw	e,h	fundamental I,II
168	w	e,h	fundamental I
183	w	e	fundamental II
203	w,d	e	fundamental I,II
240	s	±e	fundamental I
251	w,d	e	fundamental II
288	s	±e,i	fundamental I,II
305	w	e,k	fundamental I
316	m	±e	fundamental II
350	m	±e	fundamental I,II
373	w,d	±e	fundamental I,II
392	m,d	±e,k,i	fundamental I,II
438	m	e	fundamental II
441	vs	±e,k	fundamental I
458	vs,b	±e,k	fundamental I,II
506	m,sh	±e,k,i	fundamental II
531	m,sh	±e,k,i	fundamental I
631	m,sh	e,k,i	fundamental I
652	vs,sh	e,k	fundamental II
902	w,d	e,k	fundamental I
927*	vw	e	fundamental II
1046	s,d	e,k	fundamental I,II

TABLE XVI--Continued

Wave Number	Description[a]	Exciting Hg lines[b]	Interpretation
1093	w,d	e,k	fundamental II
1114	w,d	e,k	fundamental I
1169	vw,d	e,k	fundamental II
1209	m,d	e,k	fundamental I

[a]For the meaning of the abbreviations used see footnotes to Table II.

[b]The meaning of the Kohlrausch symbols are: e 4358 A, k 4047 A, i 4078 A, h 4108 A; ± indicates that the Raman band has been observed both as a Stokes and an anti-Stokes shift.

*Bands with an asterisk were not observed by Glockler and Sage (ref. 57).

TABLE XVII

TENTATIVE FUNDAMENTAL VIBRATIONAL FREQUENCIES FOR ONE ROTATIONAL ISOMER (I-FORM) OF $CF_2Cl - CFCl_2$ (in cm^{-1})[a]

Infrared			Raman	Approximate Motion
Gas	Liquid	Solid	Liquid	
			ca 80 vw	Torsion
			168 w	Rocking
			203 w	Rocking
			240 s	Rocking
			288 s	Rocking
309 m			305 w	$CFCl_2$ deformation
350 w		351 w	350 m	CF_2Cl deformation
		374 vw	373 w	$CFCl_2$ deformation
391 m		391 w	392 m	CF_2Cl deformation
442 w	ca 444 w	444 w	441 vs	$CFCl_2$ deformation
460 m	ca 461 m	461 m	458 vs	CF_2Cl deformation
531 s	532 m	530 s	531 m	C-Cl stretching
632 s	633 s	629 s	631 m	C-Cl stretching
816 vs	ca 806 vs	807 vs		C-Cl stretching
909 vs	ca 902 vs	900 vs	902 w	C-C stretching
1047 vs	1045 vs	1042 vs	1046 s	C-F stretching
1119 vs	1109 vs	1099 vs	1114 w	C-F stretching
1212 vs	1209 vs	1209 vs	1209 m	C-F stretching

[a]For the meaning of the abbreviations used see footnote to Table I.

TABLE XVIII

TENTATIVE FUNDAMENTAL VIBRATIONAL FREQUENCIES FOR ONE ROTATIONAL ISOMER (II-FORM) OF $CF_2Cl - CFCl_2$ (in cm^{-1})[a]

Infrared			Raman	Approximate Motion
Gas	Liquid	Solid	Liquid	
			ca 80 vw	Torsion
			183 w	Rocking
			203 w	Rocking
			251 w	Rocking
			288 s	Rocking
314 m			316 m	$CFCl_2$ deformation
350 w		351 w	350 m	CF_2Cl deformation
		380 w	373 w	$CFCl_2$ deformation
		395 m	392 m	CF_2Cl deformation
437 vw		437 vw	438 w	$CFCl_2$ deformation
460 m	ca 461 m	457 w	458 vs	CF_2Cl deformation
507 m	509 m	507 w	506 m	C-Cl stretching
651 s	653 s	650 s	652 vs	C-Cl stretching
816 vs	ca 806 vs	807 vs		C-Cl stretching
927 vw	ca 924 w	297 s	927 vw	C-C stretching
1041 vs	1033 vs	1031 vs		C-F stretching
1114 s		1087 s	1093 w	C-F stretching
1179 vs	1171 vs	1064 vs	1169 vw	C-F stretching

[a]For the meaning of the abbreviations used see footnote to Table I.

CHAPTER VII

INFRARED AND RAMAN SPECTRA OF $CF_2Br - CCl_2Br$

Introduction

In the present chapter infrared and Raman spectral data are reported for $CF_2Br - CCl_2Br$. Like the molecules studied in chapters V and VI, this compound is expected to exist as a mixture of rotational isomers having symmetries C_s and C_1 (see chapter I). The existence of rotational isomerism is verified by the large number of strong infrared and Raman bands observed. Sufficient data could not be obtained to interpret the spectra completely. However, a tentative list of fundamentals is given.

Experimental Results

The sample (mp 46°C) was prepared and purified in the laboratory of Professor A. L. Henne at Ohio State University. The spectra indicates that the purity is high. The infrared absorption spectrum of the gas was obtained by the procedure described in chapter II. At room temperature the compound has a vapor pressure of only 7 mm. Hence, very weak combination bands could not be recorded for the gas, even with a 1-m cell. The infrared spectrum of the sample

in a 20% solution in carbon tetrachloride was obtained in the region from 1250 to 5500 cm^{-1} with the aid of a cell of thickness 0.634 mm.

The spectral region from 650 to 1250 cm^{-1} was studied with the sample dissolved in non-polar carbon disulfide and in strongly polar nitromethane, using a cell of thickness 0.0267 mm. The infrared spectrum of the sample dissolved in carbon disulfide was also recorded in the region 350 - 700 cm^{-1}. The infrared spectrum of the solid was obtained at room temperature and at -180°C. Demountable cells with different spacers were used at room temperature, while the spectra at -180°C were obtained with the previously mentioned low-temperature cell.[13]

The compound is a solid at room temperature. In order to get the Raman spectrum of it in the liquid state, the Raman tube containing the sample was surrounded by a heating coil and heated to approximately 55°C. The Raman exposures were made as described in chapter II. However, after approximately 2 - 3 hours exposure the sample turned yellow-brown, indicating that the compound is unstable under heating and irradiation. The bromine liberated absorbed the mercury light strongly. It was necessary, therefore, to open the sealed Raman tube twice and distill off the free bromine at low pressure in order to obtain a fairly satisfactory Raman exposure. Because of these experimental difficulties, the Raman spectrum obtained is not as complete

as would have been desirable. However, all the fundamental frequencies are probably recorded. No polarization measurements could be made. Furthermore, the instability of the compound prevented infrared or Raman spectra to be obtained at high temperatures.

The infrared spectrum of the gas is shown in Figs. 30 and 31. Since only a few weak bands were found in the LiF region, this part of the spectrum is not shown. Fig. 32 shows the infrared spectrum of solid $CF_2Br - CCl_2Br$ at room temperature in the NaCl region. The wave numbers of the observed absorption maxima (or "shoulders") are listed in Table XIX; the Raman spectral data are presented in Table XX.

Interpretation

The large number of strong bands observed indicates that $CF_2Br - CCl_2Br$ exists as a mixture of rotational isomers. In accordance with what has been assumed in chapters V and VI, $CF_2Br - CCl_2Br$ is considered to be a mixture of a "trans" form having symmetry C_s and two enantiomorphic "gauche" forms having symmetry C_1. The normal vibrations of the "trans" form divide into symmetry species in the following manner: 11 a' and 7 a". The normal vibrations of the "gauche" form all belong to the same species a. Assuming the internuclear distances C-C = 1.54, C-F = 1.37, C-Cl = 1.78, C-Br = 1.98 A, and tetrahedral angles, one finds the following principal moments of inertia for the "trans" form: 756.6, 1791.3 and 1931.3 x 10^{-40} gcm^2. The axis of smallest and largest

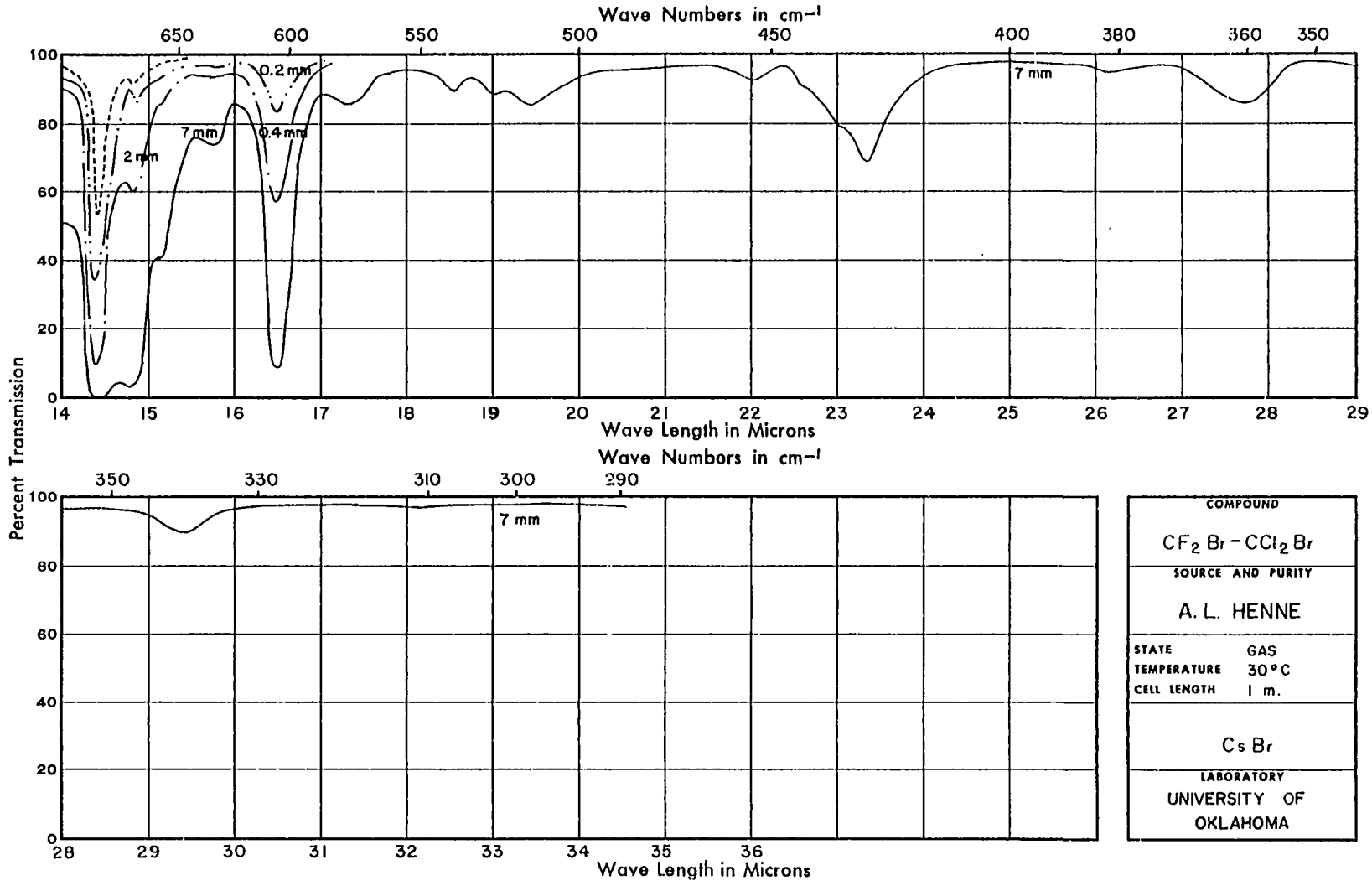

Fig. 30. Infrared Spectrum of Gaseous CF_2Br-CCl_2Br (CsBr Region)

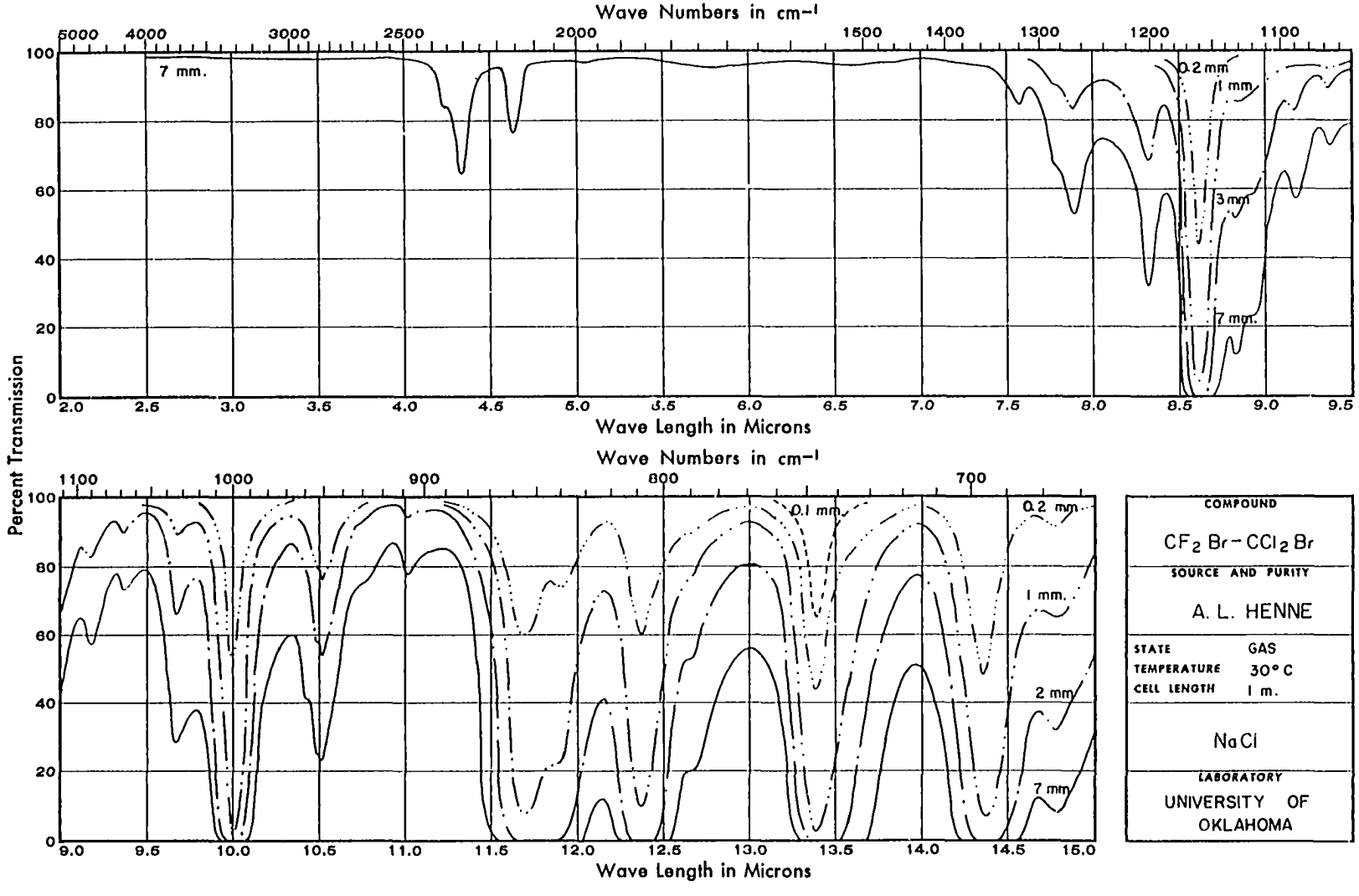

Fig. 31. Infrared Spectrum of Gaseous CF_2Br-CCl_2Br (NaCl Region)

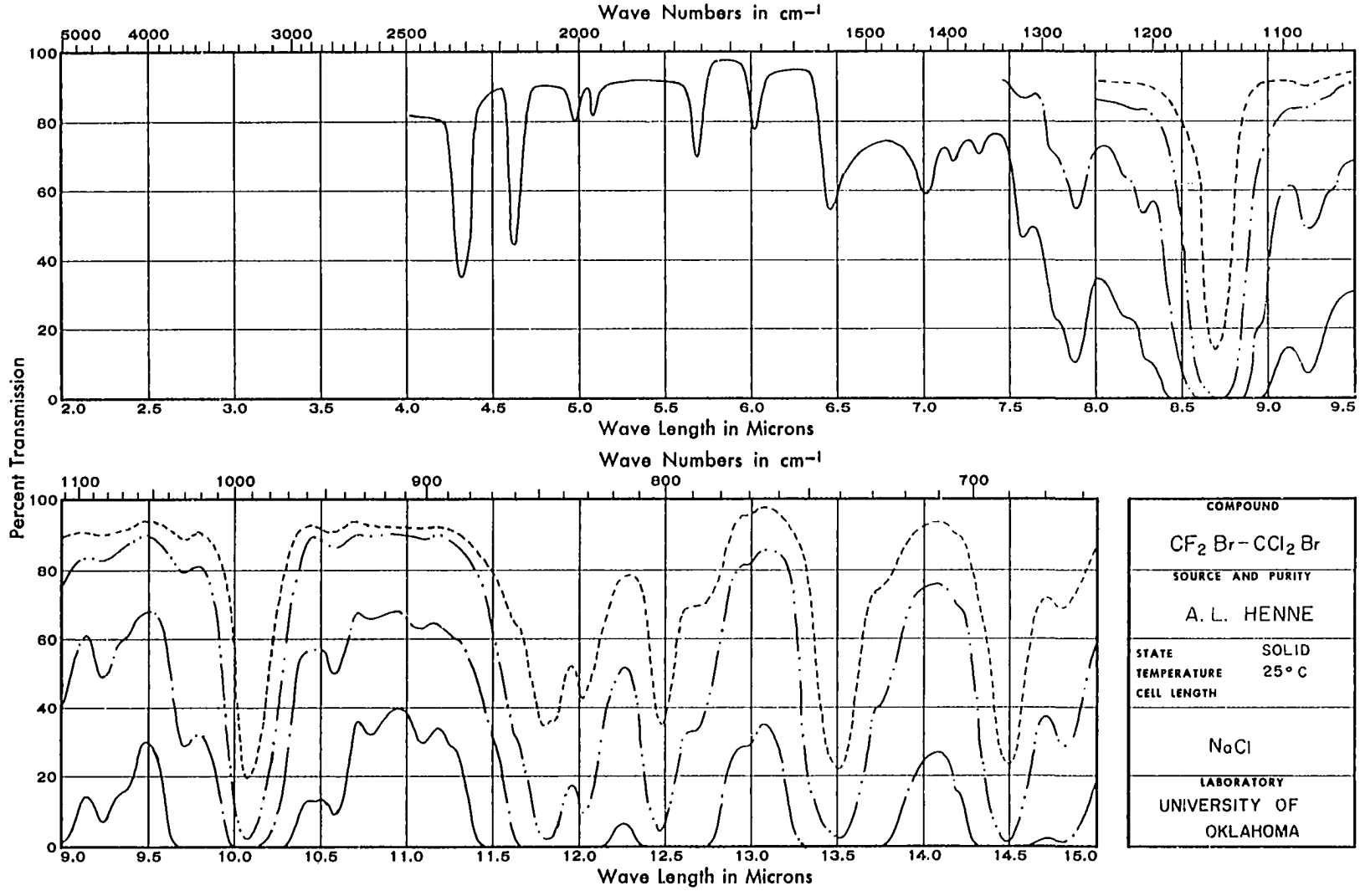

Fig. 32. Infrared Spectrum of Solid CF_2Br-CCl_2Br (NaCl Region)

moments of inertia lie in the symmetry plane, the axis of largest moment making an angle of 40°29 with the C-C bond. Thus, infrared bands of species a" should have type B contours, while bands of species a' should have contours that are hybrids of types A and C. Extrapolation from Badger and Zumwalt's curves[39] give a QQ separation of 4 cm^{-1} for type B bands, and PR separations of 6 and 5 cm^{-1} for A and C bands, respectively. No predictions can be made for the contours of the bands of the "gauche" isomer. The predicted contours for the "trans" isomer are of little value for the assignments, however, since no infrared band shows well resolved contours. This is caused in part by the close spacing of the P, Q and R branches, but undoubtedly also by strong overlapping of "trans" and "gauche" bands.

No means was found to decide which of the observed fundamentals belong to the "trans," which belong to the "gauche" and which are common to both isomeric forms. Firstly, the spectra of the gaseous and dissolved states were not significantly different from those of the solid state, as shown for the NaCl region in Figs. 31 and 32. Secondly, since the compound decomposes when heated, a possible shift of the equilibrium with temperature could not be studied. Thirdly, no appreciable intensity changes were found for the strong infrared bands in the region 650 - 1250 cm^{-1} when the compound was dissolved first in the non-polar carbon disulfide and then in the highly polar

nitromethane. Finally, comparatively few combination bands were recorded, and most of them were observed only in solution. The position of the combination bands gave, therefore, no clue as to which fundamentals belong to the same isomer (see chapters V and VI).

The number of vibrational fundamentals expected in the different spectral regions can be fairly well predicted from the structure. In the region from 1050 to 1400 cm^{-1} two fundamentals of each isomer are expected, involving C-F stretching. These bands are usually weak and diffuse in the Raman spectrum and very intense in the infrared.[14] In the region considered only the infrared band at 1162 cm^{-1} and the broad and diffuse Raman band at 1154 cm^{-1} can be assigned unambiguously as a C-F stretching fundamental. A number of medium or weak infrared bands in this region, without Raman counterparts, have all been assigned as combination bands. The very strong infrared band at 1000 cm^{-1} and the strong, diffuse Raman band at 993 cm^{-1} are also assigned as a fundamental associated with C-F stretching. Its frequency is somewhat lower than expected, indicating that the vibration does not consist of pure C-F stretching. Each of these two fundamentals are assumed to be common to both isomers.

Two very strong infrared bands are found at 856 and 851 cm^{-1} and a weak, broad Raman band at 844 cm^{-1}. They are assigned as fundamentals, one belonging to each isomer, and

are probably assiciated largely with C-C stretching.

In the region from 900 to 500 cm^{-1} four fundamentals of each isomer, involving C-Cl and C-Br stretching, are expected. Such fundamentals usually appear strong in both the infrared and the Raman spectrum.[14,63] The very strong infrared bands at 840, 808 and 747 cm^{-1} have counterparts in the Raman spectrum at 829, 801 and ca 740 cm^{-1}, respectively. They are undoubtedly all fundamentals. The fairly strong shoulder at 790 cm^{-1} has no Raman counterpart and is assigned as a combination band. It is reasonable to assign the close infrared bands at 840 and 808 cm^{-1}, and their Raman counterparts, as fundamentals of different isomers. The infrared band at 747 cm^{-1}, having a very weak, broad Raman counterpart, on the other hand, is interpreted as overlapping fundamentals of both isomers. The strong infrared bands at 696 and 676 cm^{-1} appear both to correspond to the weak, broad Raman band at 690 cm^{-1}. They are assigned as fundamentals of different isomers. Similarly, the medium intense infrared bands at 606 and 600 cm^{-1}, which are barely separated in the infrared spectrum of the liquid but are clearly separated in the spectra of the solid and the solution, and the Raman bands at 609 and 604 cm^{-1}, are assigned as a fundamental of each isomer.

In the region below 600 cm^{-1} the fundamentals involving deformation, rocking and torsion are expected, i.e. 11 fundamentals for each isomer. However, only four infrared bands sufficiently strong to be considered as fundamentals

and only 13 Raman bands are observed in this region. It appears, therefore, that most of the low fundamentals of the "trans" and "gauche" isomers overlap. The majority of these fundamentals lie below the range of the CsBr prism and have been observed in the Raman spectrum only. As mentioned earlier, experimental difficulties made it impossible to obtain a very strongly exposed Raman spectrum. Very weak fundamentals may therefore not have been observed. However, a number of the Raman bands in this region appear quite broad, indicating that they may represent overlapping fundamentals. Very little information is available to make detailed assignments in this region. The four broad Raman bands at 429, 396, 361 and 338 cm^{-1}, each having a weak infrared counterpart, are all assigned as overlapping "trans" and "gauche" fundamentals. The vibrations may be characterized roughly as deformations of the end-groups. A number of weak or very weak infrared bands in the region from 600 to 430 cm^{-1}, observed mostly in the spectrum of the solid and having no counterparts in the Raman spectrum, are all interpreted as combination bands. The fairly sharp, closely spaced Raman bands at 298 and 283 cm^{-1} of medium and weak intensity, respectively, are assigned as fundamentals belonging to different isomers. The weak Raman band at 262 cm^{-1} and the very broad and very strong Raman band at ca 235 cm^{-1} are each interpreted as overlapping fundamentals of both isomers. The medium intense, sharp Raman bands at 186 and 172 cm^{-1} are

assigned as fundamentals of different isomers. Three more low-frequency Raman bands are observed. The strong background near the exciting mercury line partly masks these bands and makes them appear very weak. The Raman bands at 118 and 92 cm^{-1} are both assigned as overlapping fundamentals. These, as well as the other fundamentals below 300 cm^{-1}, may be ascribed essentially to rocking motions. The existence of the lowest observed Raman band at ca 75 cm^{-1} is somewhat doubtful. However, it is tentatively assigned as overlapping fundamentals associated with torsion.

In terms of these fundamentals, it has been possible to interpret all the observed infrared bands, except those at 3042, 3008 and 2361 cm^{-1}, as binary combinations. All these combinations involve at least one overlapping fundamental. Some combinations of fundamentals are assigned to one isomer only. However, this may not be meaningful, since these fundamentals may actually belong to different isomers. The large number of fundamentals, particularly in the low-frequency region, makes different interpretations possible for many of the combination bands. Moreover, since most of the weak combination bands are observed in the dissolved or solid state only, a considerable discrepancy between the observed and calculated frequencies may occur. The bands at 3042, 3008 and 2361 cm^{-1} can readily be interpreted as ternary combination bands.

The tentative fundamentals are listed in Table XXI,

and the interpretations of the observed infrared and Raman bands are listed in Tables XIX and XX.

Since the infrared and Raman spectra could not be recorded at high temperatures, no information is available about the enthalpy difference, ΔH^{o}, between the isomers in either the gaseous or the liquid state. Furthermore, no significant change in the intensities of the infrared bands were observed when the sample was dissolved first in carbon disulfide and then in nitromethane. The dilute solution method of Powling and Bernstein[28] for determining the energy difference between the isomers could therefore not be used. According to Onsager's dielectric theory,[43] a displacement of the isomeric equilibrium with the dielectric constant of the solvent is expected when the isomers have different dipole moments. If the following values are assumed for the bond moments:[58] $\mu_{C-F} = 1.41$, $\mu_{C-Cl} = 1.46$ and $\mu_{C-Br} = 1.38$ D, simple vector addition gives approximately the same dipole moments for the "trans" and the "gauche" forms. It is, therefore, not surprising that no displacement of the isomeric equilibrium was observed.

It was mentioned that no significant differences were observed between the infrared spectra of the gaseous and dissolved states and the spectrum of the solid. Moreover, the spectrum of the solid obtained at -180°C was quite similar to that obtained at room temperature, apart from somewhat sharper band contours. $CF_2Br - CCl_2Br$

therefore exists as a mixture of rotational isomers in the solid as well as in the gaseous and liquid states. Similar conclusions were drawn for the compounds reported in chapters IV - VI and for other fluorinated ethanes recently studied by Lakshmi[13] and Halley,[21] as well as for $CFCl_2$ - $CFCl_2$ studied by Kagarise.[27] The spectra of these compounds in the solid state could be studied only with the aid of a low-temperature cell, and there is some doubt if the solids were really crystalline. The present molecule, however, is a solid at room temperature. It was shown to be in a true crystalline state at room temperature in the following manner: at a temperature somewhat above the melting point, the sample was placed between two NaCl plates. It was studied under a microscope during solidification and was seen to form regular crystals. The crystalline state was further verified by observing the sample with plane polarized light. It must, therefore, be concluded that CF_2Br - CCl_2Br exists in the solid state as a mixed crystal of both isomers.

Steric considerations indicate that the "trans" and "gauche" forms may be about equally stable. The bulky halogens situated on both end-groups probably cause a considerable steric strain that is fairly similar in both isomers. The steric repulsion may explain in part the relative instability of the molecule.

TABLE XIX

INFRARED SPECTRAL DATA FOR CF_2Br - CCl_2Br (in cm^{-1})

Gas		Solution[a]		Solid		
Wave Number	Description[b]	Wave Number	Description[b]	Wave Number	Description[b]	Interpretation
340	vw					fundamental
361	w			362	w	fundamental
				ca 388	vw,b	fundamental
430	m			429	m	fundamental
				434	w	172 + 262 = 434
				443	vw	186 + 262 = 448
				453	vw	118 + 340 = 458
				516	vw,b	ca235 + 283 = ca518
523	w			525	vw	262 x 2 = 524
				538	vw	ca235 + 298 = ca533
				550	vw?	186 + 361 = 547; 118 + 429 = 547
576	w			582	vw	186 + 396 = 582
				594	w	ca235 + 361 = ca596
600	m	602	m	603	m	fundamental
606	m	610	w	609	m	fundamental
632	w	637	vw	638	w	298 + 340 = 638
661	m	652	m	656	m	ca235 + 429 = ca664; 298 + 361 = 659
676	s	671	s	674	s	fundamental
696	vs	688	vs	690	vs	fundamental

TABLE XIX--Continued

Gas		Solution[a]		Solid		
Wave Number	Description[b]	Wave Number	Description[b]	Wave Number	Description[b]	Interpretation
				705	vw	340 + 362 = 702
				728	vw	298 + 429 = 727
747	vs	738	vs	739	vs	fundamental
				772	vw	92 + 690 = 782
790	s	789	m	791	s	361 + 430 = 791
808	vs	800	vs	802	vs	fundamental
840	vs	830	vs	832	vs	fundamental
851	vs	844	vs	845	vs	fundamental
856	vs	849	vs	848	vs	fundamental
		859	w	859	vw	2 x 430 = 860
				887	vvw	92 + 802 = 894
903	w			902	vw	ca235 + 676 = 911
931	w			926	vw	186 + 747 = 933
947	w					340 + 606 = 946
951	m	943	m	945	m	262 + 690 = 952
954	w					118 + 840 = 958
958	w					361 + 600 = 961
1000	vs	984	vs	993	vs	fundamental
1034	m	1028	m	1031	m	361 + 676 = 1037
1067	w			1066	w	262 + 808 = 1070
1090	w	1081	m	1083	m	ca235 + 856 = ca1091

TABLE XIX--Continued

Gas		Solution[a]		Solid		
Wave Number	Description[b]	Wave Number	Description[b]	Wave Number	Description[b]	Interpretation
1119	m			1116	w	262 + 856 = 1118
1133	m					396 + 747 = 1143
1162	vs	1155	vs	1150	vs	fundamental
1203	m			1208	w	2 x 606 = 1212
1269	w	1267	w	1268	w	430 + 840 = 1270
1287	w	1292	w	1286	w	298 + 1000 = 1298
1321	w	1316	w	1319	w	172 + 1162 = 1334
		1361	vw	1364	vw	361 + 1000 = 1361
		1386	vw	1393	vw	ca235 + 1150 = ca1385
		1423	vw	1428	vw	429 + 993 = 1422
				1549	vw	739 + 802 = 1541
				1657	vw	2 x 832 = 1664
		1679	vw			690 + 993 = 1683
		1751	w	1759	w	603 + 1150 = 1753
		1898	vvw?			738 + 1155 = 1893
		1956	vvw	1969	vw	802 + 1150 = 1952
		1988	vw	2008	vw	2 x 993 = 1886
2162	w	2146	w	2157	w	1000 + 1162 = 2162
2309	w	2298	w	2315	w	2 x 1162 = 2324
2361	vw					
		3008	vvw			

TABLE XIX--Continued

Gas		Solution[a]		Solid		
Wave Number	Description[b]	Wave Number	Description[b]	Wave Number	Description[b]	Interpretation
		3042	vvw			

[a]Data concerning the solutions:

Region	Conc.	Solvent	Cell Thickness
350 - 1250	20%	CS_2	0.0267 mm
1250 - 5500	20%	CCl_4	0.634 mm

[b]The following abbreviations have been used: s strong, m medium, w weak, v very, b broad.

TABLE XX

RAMAN SPECTRAL DATA FOR LIQUID $CF_2Br - CCl_2Br$[a]

Wave Number	Description[b]	Exciting Hg lines[c]	Interpretation
ca 76	vw?	e	fundamental
92	vw	e	fundamental
118	w,d	e	fundamental
172	m,sh	e	fundamental
186	m,sh	e	fundamental
ca 235	vs,vb	±e,k	fundamental
262	w	±e,k	fundamental
283	w	±e	fundamental
298	m	±e,k	fundamental
338	s,b	±e,k	fundamental
361	vs,b	±e,k	fundamental
396	s,b	±e,k,i	fundamental
429	m,b	e,k	fundamental
604	m,sh	e,k	fundamental
609	m,sh	e	fundamental
690	vw,b	e	fundamental
ca 740	vvw,d	e	fundamental
801	w,d	e,k	fundamental
829	s	e,k	fundamental
ca 844	w,b	e	fundamental
992	s,d	e,k,i	fundamental
1154	w,d	e	fundamental

TABLE XX--Continued

Wave Number	Description[b]	Exciting Hg lines[c]	Interpretation
1200	vvw	e	2 x 604 = 1208

[a]The sample was heated to melting (approx. 55°C).

[b]For the meaning of the abbreviations used see footnotes to Table II.

[c]The meaning of the Kohlrausch symbols are: e 4358 A, k 4047 A, i 4078 A.

TABLE XXI

TENTATIVE FUNDAMENTAL VIBRATIONAL FREQUENCIES FOR CF_2Br - CCl_2Br[a]

Infrared			Raman			Approximate Motion
Gas	Solution[b]	Solid	Liquid	No. of isomers[c]		
			ca 75 vw?	2		Torsion
			92 vw	2		Rocking
			118 w	2		Rocking
			172 m	1		Rocking
			186 m	1		Rocking
			ca 235 vs	2		Rocking
			262 w	2		CCl_2Br deform
			283 w	1		CF_2Br deform
			298 m	1		CF_2Br deform
340 vw			338 s	2		CCl_2Br deform
361 w		362 w	361 vs	2		CCl_2Br deform
		388 vw	396 s	2		CF_2Br deform
430 m		429 m	429 m	2		CF_2Br deform
600 m	602 m	603 m	604 m	1		C-Br stretch
606 m	610 w	609 m	609 m	1		C-Br stretch
676 s	671 s	674 s		1		C-Br stretch
			ca 690 vw			
696 vs	688 vs	690 vs		1		C-Br stretch
747 vs	738 vs	739 vs	ca 740 vw	2		C-Cl stretch
808 vs	800 vs	802 vs	801 w	1		C-Cl stretch
840 vs	830 vs	832 vs	829 s	1		C-Cl stretch

TABLE XXI--Continued

Infrared			Raman	No. of isomers[c]	Approximate Motion
Gas	Solution[b]	Solid	Liquid		
851 vs	844 vs	845 vs	ca 844 w	1	C-C stretch
856 vs	849 vs	848 vs		1	C-C stretch
1000 vs	984 vs	993 vs	992 s	2	C-F stretch
1162 vs	1155 vs	1150 vs	1154 w	2	C-F stretch

[a]For abbreviations used see footnote b in Table I.

[b]For data concerning solutions see footnote a Table XIX.

[c]1 and 2 indicate that the fundamental belongs to one or two isomers, respectively.

CHAPTER VIII

CONCLUSION

It was mentioned in the introduction that the present investigation has two main purposes: (a) To study the rotational isomerism exhibited by certain fluorinated ethanes and to determine the enthalpy difference between the isomers in the gaseous and liquid states. Also to determine which isomer is the more stable in gas or liquid and in what molecular forms the compounds crystallize. Included in this part of the work was a study of the displacement of the isomeric equilibrium when the sample is dissolved in different solvents. (b) To study the vibrational spectra of these fluorinated ethanes and assign the fundamental vibrational frequencies of each isomeric form.

These two aims of the work cannot be treated independently, since the assignment of the vibrational fundamentals presumes a thorough knowledge of the rotational isomerism.

With the exception of $CF_2Br - CCl_2Br$ which is unstable and could not be studied thoroughly, the enthalpy difference between the rotational isomers in gas and liquid

was determined for all compounds. A complete assignment of fundamentals is very difficult when two isomers are present and was attempted only for CHF_2 - CHF_2 and CH_2F - CH_2F, both of which have the general structure CX_2Y - CX_2Y. The rather high symmetry of these molecules make their spectra easier to interpret than those of the remaining molecules which has the general structure CX_2Y - $CX_2'Y'$. In particular, the existence of a trans isomer in the former class of compounds, having the symmetry C_{2h} and mutual exclusion of infrared and Raman activity among the fundamentals, is a great aid in the assignments. Fairly complete assignments were carried out also for CF_2Cl - CHF_2, CF_2Br - CHF_2 and CF_2Cl - $CFCl_2$. However, since it was necessary to make a number of somewhat questionable assumptions, these assignments should be considered as more or less tentative. For CF_2Br - CCl_2Br only a quite tentative list of fundamentals has been given.

Some of the results obtained in the present study can be summarized as follows:

1. The existence of two rotational isomers in the gaseous and liquid states has been confirmed for six halogenated ethanes of structure CX_2Y - $CX_2'Y_2'$.
2. The rotational isomers of CHF_2 - CHF_2 and CH_2F - CH_2F were shown to have symmetry C_{2h} (trans) or C_2 (gauche). The compounds of structure CX_2Y - $CX_2'Y'$ were each assumed to have one isomer of symmetry C_s ("trans") and one of

symmetry C_1 ("gauche").

3. Considerable overlapping occurs between some of the corresponding vibrational modes of the two rotational isomers, causing a number of the infrared and Raman bands to appear fairly broad. However, many of the corresponding fundamentals of trans and gauche or "trans" and "gauche" isomers are well separated. This is particularly true for the bands assigned to fundamentals involving mainly C-F stretching.
4. The polar gauche molecules are found to be stabilized relative to the trans molecules on going from gas to liquid or from polar solvents to non-polar solvents, in accordance with Onsager's theory.
5. CHF_2 - CHF_2 is shown to crystallize in the pure trans form. All the remaining compounds exist as a mixture of both isomers in the solid state. CF_2Br - CCl_2Br is shown to solidify as a mixed crystal. The solids formed of the compounds CH_2F - CH_2F, CF_2Cl - CHF_2, CF_2Br - CHF_2, CF_2Cl - $CFCl_2$ are also believed to be crystalline. However, it is possible that they consisted at least in part of amorphous glasses.
6. The present work supports the assumption that steric effects are most important in determining

the relative stability of the rotational isomers. Besides the steric effects electrostatic effects, including hydrogen bonding, are undoubtedly also of importance. Meaningful potential functions for these molecules, therefore, have steric as well as electrostatic terms.

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